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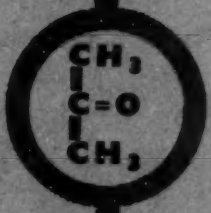

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CONJUGATION PHENOMENA IN THE 2-ARYL-*CYCLO*PROPANE-CARBOXAMIDE SERIES*

by

G. W. PEROLD

OPSOMMING

'n Vroeëre ondersoek in hierdie laboratorium het bevestig dat die onversadigde aard van die *siklo*propaanring hierdie ring in staat stel om aan konjugasie-verskynsels, wat in die reeks verbindinge in die titel genoem voorkom, aandeel te hê. Nog twee nuwe en swaar toeganklike lede van hierdie reeks is nou gesintetiseer en ondersoek.

Trans-1-metiel-2-feniel-*siklo*propaan-karboksamied is gesintetiseer, uitgaande van die onstabiele etiel-α-diasopropionaat en stireen, en sy struktuur deur osonolise en oksidasie tot *trans*-1-metiel-*siklo*propaan-1, 2-dikarboksielsuur bevestig.

Trans-2-feniel-3,3-dimetiel-*siklo*propaan-karboksamied is gesintetiseer, uitgaande van ω,ω-dimetielstireen en etiel-diasoasetaat. Twee isomere produkte word in hierdie sintese verkry en hulle aard word bespreek.

Oorweging van die ultra-violetabsorpsie van die volledige reeks van sewe gesubstitueerde *trans*-2-ariel-*siklo*propaan-karboksamiede, tesame met skaal-afbeeldings van die molekule in een vlak, toon nou dat alle konjugasieverskynsels in hierdie reeks volledig verklaar kan word in terme van steriese verhindering, te wyte aan metielgroepe, van algehele ko-planariteit tussen die benseenring, die *siklo*propaanring en die karbonielgroep van die amiedfunksie.

SUMMARY

Previous work in this laboratory has confirmed that the unsaturated nature of the *cyclo*propane ring enables it to take part in conjugation phenomena occurring in the series of compounds named in the title. Another two new and difficultly accessible members of this series have now been synthesized and investigated.

Trans-1-methyl-2-phenyl-*cyclo*propanecarboxamide was synthesized, starting from the unstable ethyl α-diazopropionate and styrene, and its structure confirmed by ozonolysis and oxidation to *trans*-1-methyl-*cyclo*propane-1,2-dicarboxylic acid.

Trans-2-phenyl-3,3-dimethyl-*cyclo*propane-carboxamide was synthesized starting from ω,ω-dimethylstyrene and ethyl diazoacetate. Two isomeric products are obtained in this synthesis and their nature is discussed.

Consideration of the ultra violet absorption of the full series of seven substituted *trans*-2-aryl-*cyclo*propanecarboxamides, in conjunction with scale diagrams of the uni-planar molecules, now shows that all conjugation phenomena occurring in this series may be fully accounted for by steric hindrance, due to methyl groups, to the attainment of full co-planarity between the benzene ring, the *cyclo*propane ring and the amide carboxyl group.

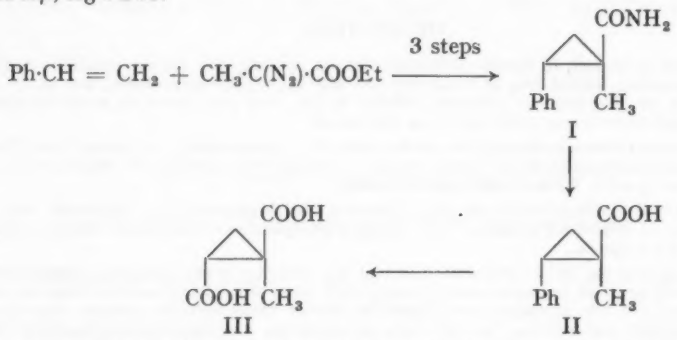
A previous study carried out in this laboratory[1] confirmed the strained nature of the *cyclo*propane ring and its ability to take part in conjugation phenomena when placed in suitable relation to other unsaturated centres. The series studied included five members of the *trans*-x-methyl-2-phenyl-*cyclo*propanecarboxamides. Further synthesis of new members of this series has now enabled greater clarity to be obtained with regard to the effects resulting from variously situated methyl substituents.

SYNTHESIS OF *TRANS*-1-METHYL-2-PHENYL-*CYCLO*PROPANECARBOXAMIDE

Starting with alanine prepared from acetaldehyde, ethyl α-aminopropionate was prepared and diazotized to yield ethyl α-diazopropionate. This very unstable reagent[2] was obtained as an impure product and was directly used as such in order

*A paper read in Pretoria at the Eighth Annual Convention of the S.A. Chemical Institute on September 1, 1954.

to incur the least amount of decomposition. A Buchner reaction[3] with styrene yielded crude ethyl 1-methyl-2-phenyl-*cyclo*propane-carboxylate. This was converted into *trans*-1-methyl-2-phenyl-*cyclo*propanecarboxamide (I), following the procedure previously described[4], and yielded a pure product, m.p. 200·5°, without any great difficulty. The ultra violet absorption spectrum (*Fig.* 1, 1) displayed a fully developed peak at 220 mμ, log ϵ 4·01 (conjugated amide)[1] and a broad (benzene) maximum at 260 mμ, log ϵ 2·38.



As impure intermediates had to be used in this synthesis, and as low yields were obtained throughout, proof was required for the validity of the structure (I). This was provided by saponifying the amide (I) to the corresponding carboxylic acid (II) and then degrading the phenyl group to a carboxyl group by ozonolysis and oxidation[5]. The product, *trans*-1-methyl-*cyclo*propane-1,2-dicarboxylic acid (III), obtained in good yield, was directly compared with an authentic sample and its identity thus confirmed.

SYNTHESIS OF *TRANS*-2-PHENYL-3,3-DIMETHYL-*CYCLO*PROPANECARBOXAMIDE.

Following the pattern of the foregoing synthesis, ω, ω-dimethylstyrene, prepared from benzyl chloride and acetone via a Grignard reaction followed by dehydration of the carbinol so formed, was subjected to a Buchner reaction with ethyl diazoacetate. As ω,ω-dimethyl-styrene contains a sterically very strongly hindered olefinic double bond, it was to be expected that addition to this double bond might proceed only with difficulty.

In full accord with this supposition, very little of the expected ester product was obtained on carrying out the Buchner reaction under varied experimental conditions. The esters obtained were, however, converted to the corresponding *trans* amides from which, after careful chromatographic separation followed by oft repeated crystallization, two very similar amides, $C_{12}H_{15}ON$, could be obtained in pure form. These two amides, m.p. 131° and 128°, displayed almost identical ultra violet absorption in ethanolic solution (*Fig.* 1, 2 and 3).

Normal addition of ethyl diazoacetate to the olefinic double bond of ω, ω-dimethyl-styrene followed by full conversion of the *cis* form to be expected in the initial ester product[4] to the *trans* form of the final amide, would, however, lead to only one amide, $C_{12}H_{15}ON$, viz. *trans*-2-phenyl-3,3-dimethyl-*cyclo*propanecarboxamide (IV). In this connection, the essentially identical ultra violet absorption spectra of the two amides indicate that they do not represent *cis* and *trans* isomers, as a marked difference is to be expected in the intensity of absorption of the *cis* as against the *trans* isomer. This has been demonstrated, e.g., for the *cis* and *trans* 2-phenyl-*cyclo*propanecarboxylic acids[6].

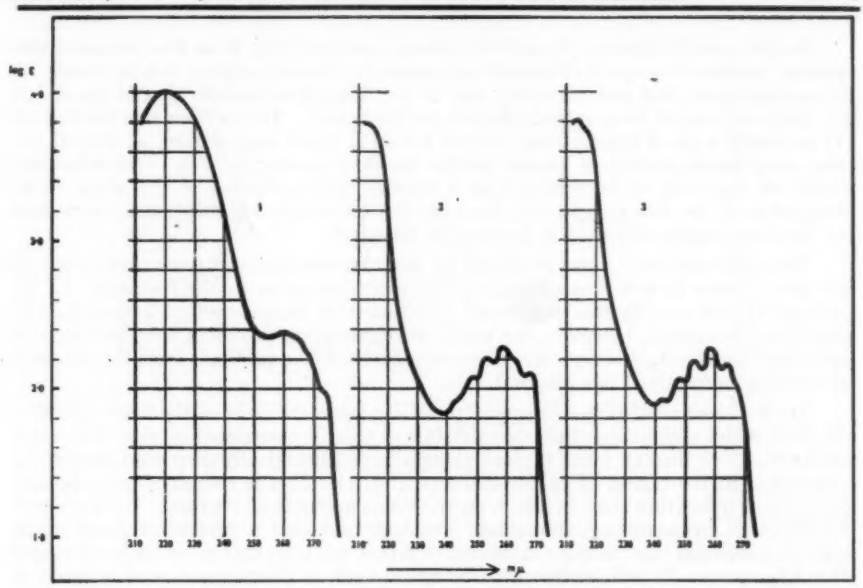
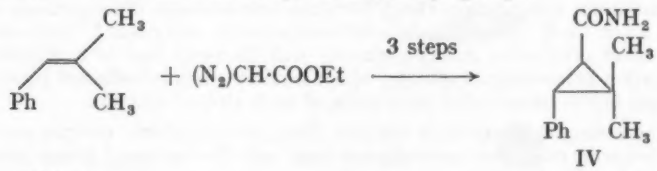
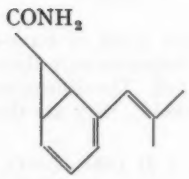


Fig. 1. Ultra violet absorbtion in ethanol of:
Trans-1-Me-2-Ph-*cyclo*proanecarboxamide.
Trans-2-Ph-3,3-diMe-*cyclo*propanecarboxamide (?), m.p. 131°.
Trans-2-Ph-3,3-diMe-*cyclo*propanecarboxamide (?), m.p. 128°.

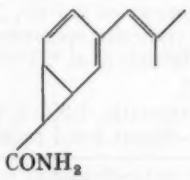
The possibility must be considered that the olefinic double bond in ω, ω-dimethylstyrene may be too strongly hindered for addition to take place at this bond and that the products may therefore have resulted from the known addition of the diazo ester to the aromatic "double bonds" of the benzene nucleus[7]. In this event two different products, (V) and (VI), may arise, bearing in mind two Kekulé forms for the arrangement of the aromatic "double bonds" and assuming no addition to such a "double bond" when substituted by the isobutenyl group.



IV



V



VI

Inspection of formulae (V) and (VI) shows, however, that these two non-aromatic systems contain two quite differently arranged patterns of olefinic double bonds, as the *cyclo*propane ring now replacing one of the original aromatic "double bonds" is not fully equivalent to a normal olefinic double bond[8]. The system represented by (V) possesses a set of three olefinic double bonds in linear conjugation, as against the cross-conjugated pattern of olefinic double bonds occurring in (VI). This difference would be expected to be reflected in a notable differentiation of the ultra violet absorption of the two compounds, whereas the ultra violet absorption as measured for the two amides obtained is practically identical.

Degradations with ozone, modelled on that described above, were carried out on the two amides in order to obtain further information as to their structures. In contrast to the smooth reaction found in the case of *trans*-1-methyl-2-phenyl-*cyclo*propanecarboxamide, however, the yields of degradation products were low in both cases and it was not possible to obtain meaningful reaction products from the amounts of starting materials at our disposal.

In the absence of direct chemical proof for the structures of these two amides, the ultra violet absorption of the two substances may be considered by way of internal evidence. Both display quite typical, though hypsochromically displaced, benzenoid absorption in the region of ca 240-270 mμ (*Fig.* 1). This is therefore provisionally accepted as indicating that, in effect, these two compounds do represent the 2-phenyl-3,3-dimethyl-*cyclo*propanecarboxamide structure and that a somewhat more subtle type of isomerism may here be involved. Further work on this problem is envisaged at a later stage. It will furthermore be noted that no short wave peak appears at 220 mμ. The molar extinction at 220 mμ is here only one quarter of that found for a fully developed conjugated amide maximum (log ϵ 3·4 against 4·0).

DISCUSSION

In considering the ultra violet absorption characteristics of the five *trans*-x-methyl-2-phenyl-*cyclo*propanecarboxamides previously obtained[1], it appeared that a hyperconjugation effect associated with the 1,2-carbon-carbon-bond of the *cyclo*propane ring might account for the effects noted. The present findings regarding the ultra violet absorption of the new 1-methyl- and 3,3-dimethyl-derivatives of this series, however, now make possible a re-interpretation of these effects and lead to a fully satisfactory explanation of the effects found for all the members of this series.

A maximum conjugation effect between two or more chromophoric centres is obtained when these various centres are contained in one plane[9]. Any substitution or other effect preventing full co-planarity will therefore lead to a diminished state of conjugation between such centres, which would in turn be reflected by corresponding changes in the ultra violet absorption of such altered systems.

In the series of compounds studied, three chromophoric centres are involved, viz. the benzene ring, the *cyclo*propane ring and the carbonyl group contained in the terminal amide function.

Scale diagrams have now been constructed for the series of *trans*-compounds concerned and are reproduced in *Figs.* 2-6*. In these diagrams only those hydrogen atoms which may be sterically operative are shown in full. The dimensions used are based on data from Braude *et al.*[9], Pauling[10] and Rodd[11]; they are the following, in Ångstrom units:—

Bond lengths: C$_7$C aromatic, 1·39; C-C single, 1·54; C-H 1·09; C=O, 1·22; C-N 1·47; N-H 1·00. Co-valent bond radii: hydrogen, 0·31; methyl 1·39; oxo 1·10.

*As the *trans*-2-(*m*- and *p*-Me-phenyl)-*cyclo*propanecarboxamides clearly are not sterically hindered structures, they are not represented.

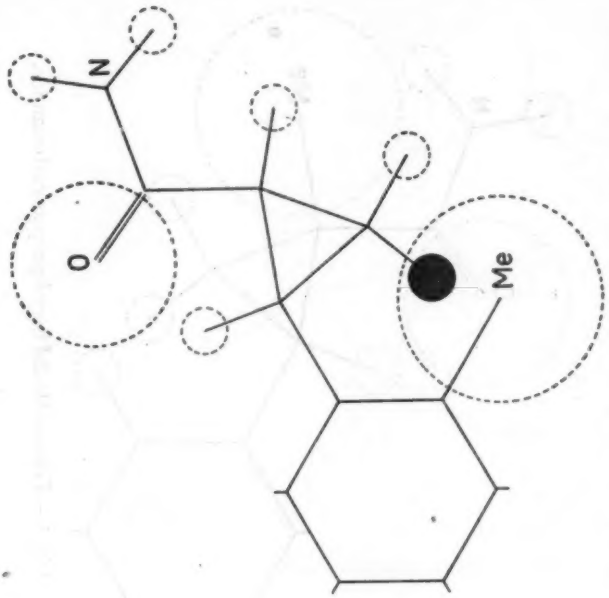


Fig. 3.—*Trans*-2-(o-Me-phenyl)-*cyclo*propanecarboxamide.

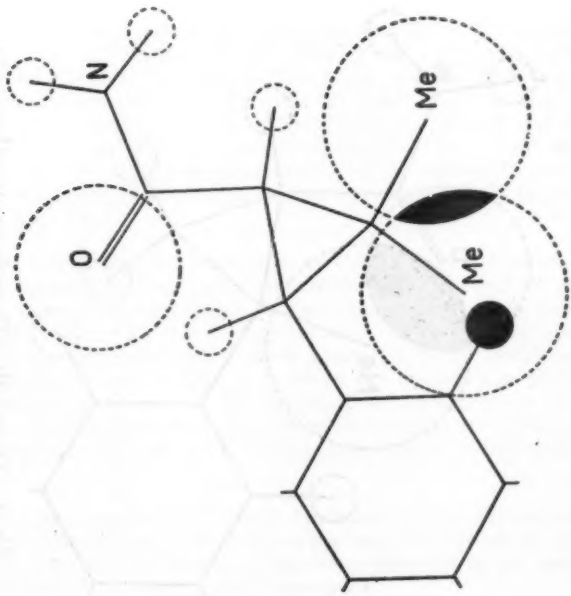


Fig. 2.—*Trans*-2-Ph-3,3-diMe-*cyclo*propanecarboxamide

Fig. 4.—*Trans*-2-Me-2-Ph-*cyclo*propanecarboxamide.

Fig. 5.—*Trans*-1-Me-2-Ph-*cyclo*propanecarboxamide.

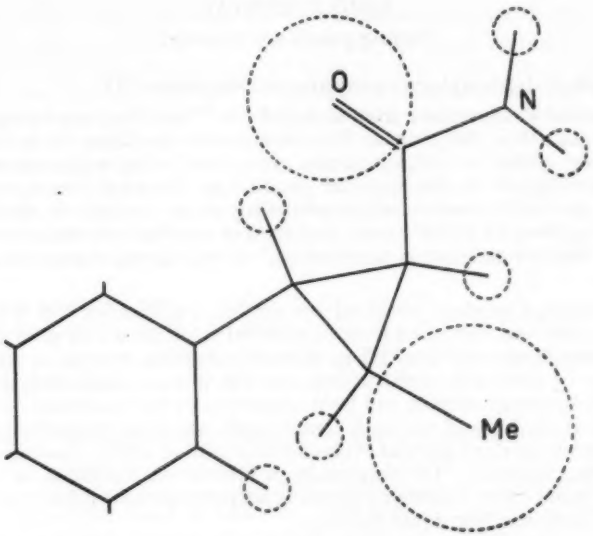


Fig. 6.—*Trans*-2-Ph-3-Me-*cyclo*propanecarboxamide.

Inspection of the diagrams shows that a full overlap occurs between the 3-*gem*-dimethyl groups and the ortho-hydrogen atom in the 2-phenyl-3,3-dimethyl-derivative (*Fig.* 2) and between the *ortho*-methyl group and a 3-hydrogen atom in the 2-(*o*-methyl-phenyl)-derivative (*Fig.* 3), while the 2-methyl group markedly overlaps the oxo group of the amide function in the 2-methyl-2-phenyl-derivative (*Fig.* 4). No such overlapping occurs in the 1-methyl-2-phenyl (*Fig.* 5) and the 2-phenyl-3-methyl derivatives (*Fig.* 6). The attainment of full coplanarity will therefore be prevented by overlapping of atoms and/or atomic groups only in the three instances represented by *Fig.* 2-4.

On relating the ultra violet absorption of the full series of seven *cyclo*propanecarboxamides, recorded in *Fig.* 1 and previously[1], with these scale diagrams, it is clear that the ultra violet absorption characteristics of all seven members of this series are in full accord with this interpretation. The short wave absorption peak (log ϵ ca 4), representing a conjugated amide group[1], is clearly developed in all cases except those corresponding to *Figs.* 2-4, where the conjugation effect is therefore suppressed by steric interference. The conjugation characteristics of this series of compounds thus parallel the similar characteristics found in other series of structures, such as the ionones and the 1-acetyl-2-methyl-*cyclo*hexenes[9] as well as the substituted acetophenones[12].

It is therefore suggested that steric hindrance to the attainment of full coplanarity of the benzene ring, the *cyclo*propane ring and the amide group provides a full explanation for the conjugation phenomena observed in the new series of the *trans*-x-methyl-2-phenyl-*cyclo*propanecarboxamides.

EXPERIMENTAL

(Melting points are corrected)

Trans-1-methyl-2-phenyl-*cyclo*propanecarboxamide (I)

Pure alanine was prepared from acetaldehyde[13] and then converted into ethy α-amino-propionate[14] in 50% yield. Diazotization of the latter in 5-12 g. portions gave a highest yield of 15% of crude, undistilled ethyl α-diazopropionate. As attempted distillation of this material resulted in the total decomposition of the diazo ester, the crude product, which according to the amount of nitrogen evolved on heating was from ca 40-90% pure, was used in the Buchner reaction with styrene without any further attempt at purification. A typical experiment was carried out as follows:—

The diazotized product obtained by careful diazotization[2] of 6·0 g. ethyl α-amino-propionate was recovered from its ethereal solution as 1·01 g. of yellow liquid. This was immediately added to 1·7 g. of freshly distilled styrene, a pinch of Pyrex glass powder (−100+200 mesh) added and the mixture cautiously heated under reflux after a simple gasometer had been connected to the condenser. The evolution of gas set in at *ca.* 55° and the bath temperature was then gradually raised to 150° during 2 h., when no more gas was evolved and a total of 222 ml. (ambient conditions) of gas had been collected. On evaporating a filtered ether solution of the products, a residue of crude ethyl 1-methyl-2-phenyl-*cyclo*propanecarboxylate was obtained as a yellowish sweet smelling liquid (2·67 g.).

This crude ester (4·83 g.) was heated under reflux with 3·5 g. KOH, 3·5 ml. water and *ca.* 5 ml. ethanol for 4 h.; 20 ml. water was then added and distilled off and this was repeated once more. Insoluble by-products were removed by extraction with ether (4 x 25 ml.) and the clear aqueous solution acidified (HCl) and extracted with ether (3 x 25 ml.). Evaporation of the ether gave a viscous residue of 0·925 g. acidic product.

The acidic product was refluxed with 3 ml. pure[15] thionyl chloride for 2 h. and the cooled solution carefully added to 20 ml. ice-cold concentrated ammonia liquor. The reaction mixture was allowed to stand at room temperature and then extracted with ether. The residue from the ether extract was sublimed for 10 h. at 150°/0·1 mm. to yield 0·434 g. crude sublimed *trans*-1-methyl-2-phenyl-*cyclo*propanecarboxamide (I), m.p. up to *ca.* 170°.

This crude amide (790 mg.) was adsorbed on a column of 25 g. alumina (BDH) and eluted with benzene+ethanol (4+1). After the first 40 ml. eluate containing 63 mg. oily crystals had been discarded, a further 150 ml. of this solvent eluted 637 mg. crystals. Two crystallizations of this material from ethanol+ligroin gave 260 mg. pure product as glistening platelets, m.p. 200·5°. A sample was sublimed at 150°/0·1 mm. for analysis.

Found: C, 75·59; H, 7·67;
calcd. for $C_{11}H_{13}ON$: C, 75·40; H, 7·48%.

The ultra violet absorption in ethanol showed the following maxima: ($m\mu/\log \epsilon$) 220/4·01, 260/2·38, 274/1·97 (shoulder). (*Fig.* 1,1).

Ozonolysis and oxidation to *trans*-1-methyl-*cyclo*propane-1,2-dicarboxylic acid (III.)

The pure amide (105 mg., m.p. 200·5°) obtained above, was refluxed with 1 g. KOH in 10 ml. water for 9 h. The clear solution was then extracted three times with ether, acidfied with 10 ml. 10 N HCl and the acid product taken up in ether and recovered as 104 mg. of acid (*trans*-1-methyl-2-phenyl-*cyclo*propane-

carboxylic acid (II)). The crude acid was crystalline and melted sharply at 79-80°.

This was dissolved in 20 ml. pure acetic acid and crude ozonized oxygen (2·4 vol.% O_3) bubbled through at a rate of 0·2 l./min. for 4 h. at 20°. After adding 6 ml. 10% w/v H_2O_2 the clear solution was evaporated to dryness on a steam cone. The residue was treated with another 3 ml. 5% w/v H_2O_2 and dried as before. Finally 2 ml. water was added and the solution dried on the steam cone again to yield 61 mg. colourless crystalline residue. A small amount of insoluble impurity was removed by extracting the main material with methyl ethyl ketone. Crystallization from methyl ethyl ketone+benzene yielded, after drying *in vacuo* at 80°, 38 mg. colourless prisms, m.p. 168·5-169·5°. A final crystallization from 0·15 ml. water gave 32 mg. pure product melting sharply at 170·5°. The product was sublimed at 150°/0·02 mm. for analysis.

Found: C, 49·91; H, 5·57%; Eq. wt., 74;
calcd. for $C_6H_8O_4$: C, 50·00; H, 5·60%; Eq. wt., 72 for 2 x COOH.

A mixture with pure authentic *trans*-1-methyl-*cyclo*propane-1,2-dicarboxylic acid (see below) gave no depression of the m.p.

Authentic *trans*-1-methyl-*cyclo*propane-1,2-dicarboxylic acid

Through the generous co-operation of the Armour Research Foundation, Chicago, a sample of authentic *trans*-1-methyl-*cyclo*propane-1,2-dicarboxylic acid was obtained. This material melted at 166-170°. One crystallization from methyl ethyl ketone+benzene and two crystallizations from water gave prisms of constant m.p. which were sublimed at 150°/0·05 mm. to give the pure reference sample, m.p. 170·5°.

Found: C, 50·28; H, 5·55%; Eq. wt., 73;
calcd. for $C_6H_8O_4$: C, 50·00; H, 5·60%; Eq. wt., 72 for 2 x COOH.

***Trans*-2-phenyl-3,3-dimethyl-*cyclo*propanecarboxamide (IV).**

A normally executed Grignard synthesis using benzyl magnesium chloride (1·3 mole scale) and acetone, gave benzyl dimethyl carbinol, distilling at 68-71°/3 mm., n_D^{14} 1·519 (lit. 1·518) in 80% yield. The carbinol (36 g. portions) was dehydrated by refluxing for 90 min. with 1·5 g. freshly fused potassium hydrogen sulphate and 0·3 g. hydroquinone at 150-200 mm. pressure in a bath kept at 175° and then distilling off the crude ω,ω-dimethyl-styrene and water at 79-83°/21 mm. Benzene was added, the upper layer washed with alkali, dried and distilled. The yield of ω,ω-dimethyl-styrene, collected at 68-71°/15mm., n_D^{32} 1·5135, was *ca.* 45%.

Found: C, 90·59; H, 9·17;
calcd. for $C_{10}H_{12}$: C, 90·83; H, 9·15%.

As ethyl diazoacetate reacted with this styrene only with difficulty, the use of copper as catalyst[4] was attempted. The decomposition of the reagent was then, however, too violent for useful application. The procedure finally worked out was the following:—

A mixture of 14·05 g. ω,ω-dimethyl-styrene, 17·2 ml. pure ethyl diazoacetate and a little Pyrex glass powder (−100+200 mesh) was cautiously warmed in a bath under reflux, with provision for measuring the evolution of gas, until the main reaction had ceased and 3·5 l. (ambient conditions) of nitrogen had been released at a highest bath temperature of 126°. The reaction product was distilled up to 200° 0·4 mm., the total distillate (*ca.* 18 g., containing *ca.* 10 g. unchanged ω,ω-dimethyl-styrene) refluxed with 10 g. KOH, 20 ml. water and 70 ml. ethanol for 13 h. and then distilled with steam until 1 l. aqueous condensate had been collected. The

alkaline residue was extracted twice with ether, acidified with 33 ml. 10 N HCl and the acid products collected in ether which was then removed to yield the acids as 2·436 g. of an amber coloured syrup. This was refluxed for 90 min. with 14 ml. thionyl chloride and the amide then formed in the usual manner. Ether extraction yielded the crude amides as 1·818 g. of brown syrup which partially crystallized on storage.

The mixture of amides was adsorbed from benzene solution on to 60 g. alumina (BDH) and eluted to yield the following fractions of 50 ml. eluate each.

Fraction	*Solvent*	*Yield*	*Remarks*
1 — 4	Benzene	190 mg.	Syrup
5 — 8	Benzene+Ether (4+1)	52 mg.	Syrup
9	Benzene+Ether (1+1)	74 mg.	crystals, m.p. 110-120°
10	,,	201	crystals, m.p. 113-119°
11	,,	124	crystals, m.p. 100-107°
12	,,	84	crystals, m.p. 75-80°
13	,,	77	crystals, m.p. 87-91°
14	,,	69	crystals, m.p. 94-103°
15	,,	58	crystals, m.p. 93-117°
16	,,	53	crystals, m.p. 101-115°
17	Ether	56	crystals, m.p. 100-115°
18	,,	53	crystals, m.p. 105-115°
19	,,	39	crystals, m.p. 107-120°
20	,,	31	crystals, m.p. 105-115°

(A further 489 mg. of syrupy products was eluted with ether+methanol and discarded).

It is clear from the m.p.s given that two substances were eluted in fractions 9-20. These were obtained in pure form by working up selectively combined fractions.

Fractions 9-11.

The combined products (399 mg.) were crystallized four times, alternately from benzene+ligroin and from ethanol+ligroin, then sublimed at 110°/0·05 mm. and crystallized another four times as before to yield 70 mg. glistening colourless platelets, m.p. 131°. A sample for analysis was sublimed at 110°/0·05 mm.

Found: C, 75·90; H, 7·90;
calcd. for $C_{12}H_{15}ON$: C, 76·16; H, 7·99%.

Ultra violet absorption was determined (Zeiss Opton) in ethanol: λ_{max} (mμ/log ϵ) 212/3·79, 248/2·08, 254/2·20, 258/2·28, 268/2·09. (*Fig.* 1, 2).

Fractions 15-20.

The combined products (290 mg.) were crystallized three times from benzene+ligroin and once from alcohol+water to yield glistening flat needles with a sharp m.p. remaining constant at 128°. A mixture with the amide, m.p. 131°, obtained from fractions 9-11, melted at 100-104°*. A sample for analysis was sublimed at 110°/0·04 mm.

*In preliminary experiments, the amide preparation obtained without employing chromatography, yielded a similar mixture, m.p. *ca.* 104°, which could not be purified to a higher m.p. by crystallization only.

Found: C, 76·07; H, 7·86;
calcd. for $C_{12}H_{15}ON$: C, 76·16; H, 7·99%.

Ultra violet absorption (Zeiss Opton) in ethanol: λ_{max} (mμ/log ϵ) 214/3·81, 248/2·06, 253/2·18, 258/2·27, 264/2·15. (*Fig.* 1, 3).

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Scientific and Research Department,
ISCOR,
Pretoria.

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FUNCTIONAL AND STRUCTURAL CHARACTERISTICS OF GEIGERIN*

by

G. W. PEROLD

OPSOMMING

Dit is reeds bekend dat die bitterstof, geigerin, watervrye vorm $C_{15}H_{20}O_4$, 'n laktoon- en 'n ketoongroep bevat. Die vierde suurstoffunksie word nou deur chemiese en fisiese bewysvoering as 'n hidroksielgroep karakteriseer. Ook word die aanwesigheid van 'n etileniese dubbelbinding in konjugasie met die ketoongroep aangetoon. Dit volg dus dat die molekuul bisiklies is.

Dehidrogenering oor palladium-kool katalis van katalities gereduseerde geigerin lewer 'n enkele rein blou asuleen met die samestelling $C_{14}H_{16}$. Dit word aangetoon dat hierdie asuleen òf identies met òf baie na verwant aan kamasuleen, 1, 4-dimetiel-7-etiel-asuleen, is.

Deur geigerin eers met litiumaluminiumhidried te reduseer en dan te dehidrogeneer word twee verdere asulene verkry. Die eienskappe van hierdie drie asulene word in verband met die waarskynlike skeletstruktuur van die geigerinmolekuul bespreek.

SUMMARY

The bitter principle, geigerin, anhydrous form $C_{15}H_{20}O_4$, was known to possess a lactone and a ketone group. The fourth oxygen function is now shown by chemical and physical characterization to be hydroxylic, while the presence of an ethylenic double bond in conjugation with the ketone group is furthermore demonstrated. The molecule is therefore bicylic.

Dehydrogenation of catalytically reduced geigerin over palladium on charcoal yields a single pure blue azulene of the composition $C_{14}H_{16}$. This azulene is shown to be either identical with or closely related to chamazulene, 1, 4-dimethyl-7-ethyl-azulene.

Two further azulenes are obtained by dehydrogenating geigerin after prior reduction with lithium aluminium hydride. The properties of these three azulenes are discussed with regard to the probable skeletal structure of the geigerin molecule.

The bitter principle, geigerin, was first isolated by Rimington and Roets[1] from the vomiting bush, *Geigeria aspera* Harv., in which it occurs in association with the suspected poisonous principle, vermeeric acid. These authors demonstrated that geigerin, anhydrous form $C_{15}H_{20}O_4$, contains one lactone group and one ketonic group; they were, however, unable to indicate the nature of the fourth oxygen function in the molecule. On distillation over zinc dust at 700° some naphthalene was obtained. Permanganate oxidation of geigerin led to extensive degradation of the molecule with the formation of an acid $C_{10}H_{14}O_4$. Further oxidations of geigerin were carried out by de Waal[2], who with nitric acid obtained a monobasic dilactonic acid, $C_{15}H_{18}O_6.H_2O$; permanganate oxidation of this compound, as well as of geigerin, led to the formation of oxalic acid. Both groups of workers noted the ready formation of acetaldehyde from geigerin under acidic conditions.

Rimington and Roets[1] considered geigerin to be identical with pyrethrosin, from *Chrysanthemum cinerariaefolium*. The non-identity of these two compounds was however established, without direct comparison, by Schechter and Haller[3].

In the present study, geigerin was isolated anew from *Geigeria aspera* Harv., using a somewhat changed procedure, in 0·04% yield based on air-dried plant material. The pure substance agreed in all respects with the description given by Rimington and Roets[1], except in that the optical rotation (mean value for $[\alpha]_D$ -64°) remained the same in ethanol, chloroform and ethyl acetate. Elementary analysis and lactone titration confirmed the empirical composition of the anhydrous product as being $C_{15}H_{20}O_4$.

*A paper read in Pretoria at the Eighth Annual Convention of the S.A. Chemical Institute on September 3, 1954.

Although a crystalline acetate could not be obtained from geigerin on a preparative scale, the presence of one hydroxyl group could now be established by analytical acetylation. This was confirmed by the occurrence of a strong absorption band at 2·83 μ in the infra red absorption spectrum of the anhydrous material (*Fig.* 1).

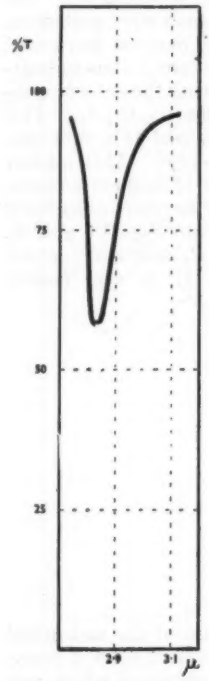


Fig. 1.—Infra red absorption of geigerin.

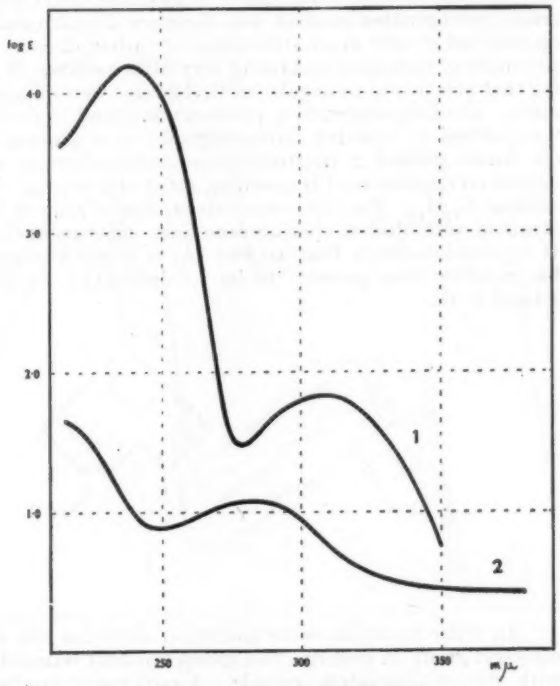


Fig. 2.—Ultra violet absorption of:
1. Geigerin in ethanol.
2. Catalytically hydrogenated geigerin in ethanol.

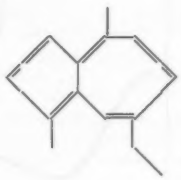
The ultra violet absorption of geigerin in ethanol (*Fig.* 2,1) showed a sharp maximum at 239 mμ, log ϵ 4·19 and a broad maximum at 310 mμ, log ϵ 1·83, thus typically representing the absorption of an α,β- or β,β-disubstituted α,β-unsaturated ketone[4]. (It may be noted that the preparation by Rimington and Roets[1] of a *red* 2,4-dinitrophenylhydrazone from geigerin also supports this conclusion).

As geigerin has now been found to give no colour reaction with tetranitromethane, it follows then that no other ethylenic double bonds are present and that the carbon skeleton of the geigerin molecule is *bicyclic*. A possible tricyclic structure, involving a *cyclo*propane ring instead of an ethylenic double bond and therefore analogous to the structure of aromadendrene[5], seems unlikely on the basis of the ultra violet absorption mentioned above, as a chromophoric system of this nature would not exhibit the typical maximum found at 239 mμ, log ϵ 4·19[6].

After thus accounting for the functional features of the geigerin molecule, it next became necessary to ascertain the nature of the ring systems contained in this

molecule. This was achieved by the catalytic dehydrogenation of variously reduced products derived from geigerin.

In a mixture of butanol and acetic acid, geigerin absorbed two moles of hydrogen over Adams' platinum catalyst. The product was a mixture of syrupy and crystalline substances from which pure components could not readily be obtained. The crude hydrogenated product was therefore dehydrogenated as such over palladium on charcoal at 280° in an atmosphere of carbon dioxide. The gas evolved was found to consist of hydrogen containing very little methane (3 mole per cent.), thus indicating that practically no angular methyl groups were eliminated during the dehydrogenation. The dehydrogenation product was found to be an azulene (A), $C_{14}H_{16}$. This was purified by repeated chromatography over alumina and obtained as a pure blue oil, which yielded a trinitrobenzene adduct melting at 133·5-135°. This adduct caused no depression of the melting point of a mixture with that of authentic chamazulene, $C_{14}H_{16}$. The ultra violet absorption of azulene (A) is furthermore essentially identical with that of chamazulene (*vide* experimental section and *Fig.* 3,1 and 4). It is therefore likely that azulene (A) is either identical with chamazulene, which has recently been proved[7] to be 1,4-dimethyl-7-ethyl-azulene (I), or very closely related to it.



I

In order to obtain some indication as to the site and nature of the lactonized carboxyl group in geigerin, this group was first reduced to a hydroxy-methyl group with lithium aluminium hydride. A mixture of products was obtained which was separated into a less water-soluble and a more water-soluble reduced product. These were then separately dehydrogenated over palladium on charcoal as before.

The less water-soluble, and therefore less polar and presumably less completely reduced product, on dehydrogenation evolved a gas, mainly hydrogen, containing rather more methane (8 mole per cent.) than that obtained from catalytically reduced geigerin.

The hydrocarbon products could here be separated into two distinct azulenes. One (B) was pure blue in colour and gave a trinitrobenzene adduct which melted at 135-137°, but was identical neither with the similar adduct derived from azulene (A) nor with that of chamazulene, even though the ultra violet absorption of the three purified azulenes was practically identical (*Fig.* 3). As concordant analytical results have not to date been obtainable on this azulene, its composition can only be discussed at a later opportunity. The other azulene (C) was blue with a tinge of mauve in colour and gave a trinitrobenzene adduct m.p. 159-160°, the composition of which indicates that the parent azulene would be represented by $C_{15}H_{18}$. The ultra violet absorption of azulene (C) shows a decided bathochromic shift relative to that of azulene (A) and chamazulene (*Fig.* 3). The nature of this shift is considered below.

The more water-soluble, and probably therefore more completely reduced, reduction product on dehydrogenation evolved a gas which contained very much more methane (30 mole per cent.) than in the instances mentioned above. The hydrocarbon products yielded the same azulenes (B) and (C) isolated in the foregoing experiment, although azulene (C) was now relatively less abundant, in accordance with the more extensive formation of methane during the dehydrogenation.

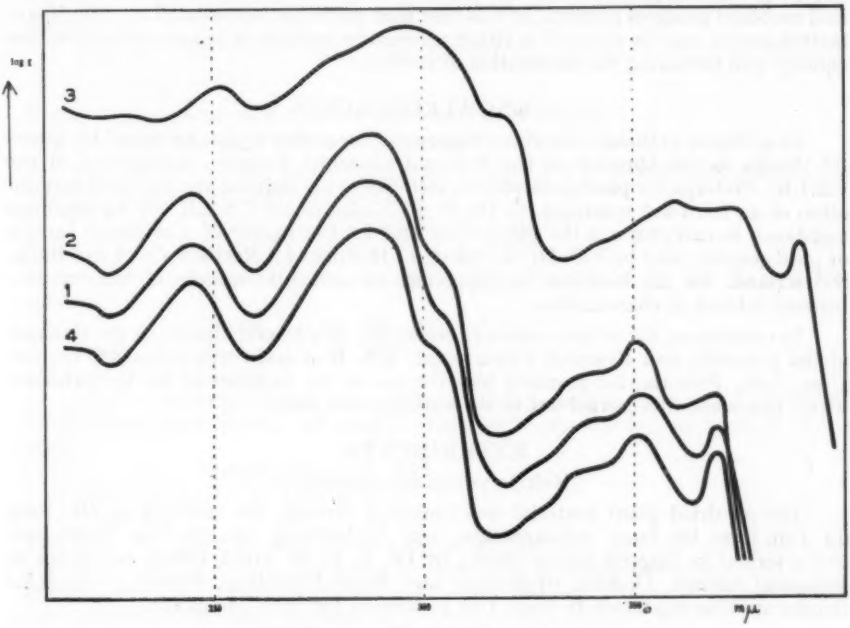


Fig. 3.—Ultra violet absorption in ligroin of:
1. Azulene (A) ex TNB adduct, m.p. 133-5-135°.
2. Azulene (B) ex TNB adduct, m.p. 135-137°.
3. Azulene (C) ex TNB adduct, m.p. 159-160°.
4. Chamazulene ex authentic TNB adduct.

While it has not yet been possible conclusively to identify any one of the three azulene hydrocarbons (A), (B) or (C) with azulenes of known structure, some generalized conclusions may be drawn as to the probable types of structure involved.

In the case of azulene (A) it is clear that one carbon atom was lost during the dehydrogenation. As catalytic hydrogenation of the type employed in this case would not normally reduce a lactone group, this loss probably involves the elimination of a molecule of carbon dioxide from the lactone group. It is furthermore clear that this azulene is closely related to chamazulene, and may indeed be identical with it. The long wave maximum at 370 mμ in the ultra violet absorption spectrum constitutes additional proof[5] that azulene (A) is substituted in uneven positions, at least as far as the five-membered ring of the molecule is concerned.

The decided bathochromic shift in the ultra violet absorption of azulene (C), $C_{15}H_{18}$, containing all the carbon atoms of the parent geigerin molecule, may indicate

that the additional methyl group, here representing the lactonized carboxyl group in geigerin, is directly attached to the nucleus. The retention of the long-wave absorption maximum in the ultra violet, here at 390 mμ, indicates that the 2-position is, however, still unsubstituted. In this connection the possibility of a migration of a methyl group during the course of the dehydrogenation must be borne in mind. The finding that the formation of methane is markedly greater when the more fully ($LiAlH_4$) reduced geigerin derivative is dehydrogenated, indicates that the lactonized carboxyl group of geigerin, in this case then probably represented by a hydroxymethyl group, may be situated in either an angular position or in some other position equally well favouring the elimination of methane.

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EXPERIMENTAL

(Melting points are corrected.)

The air-dried plant material was obtained through the courtesy of Mr. Tom du Toit from his farm, Schaapplaats, near Wolwehoek, Orange Free State, and characterised as *Geigeria aspera* Harv., by Dr. L. E. W. Codd, Officer in Charge of Botanical Survey, Division of Botany and Plant Pathology, Pretoria. Grateful thanks are also expressed to these two gentlemen for their assistance.

Extraction

The air-dried plant material (15·5 kg.), comprising the complete plants, was roughly broken up to pass a 1 inch sieve and then covered with absolute alcohol for three days. The green extract was concentrated *in vacuo* to a volume of *ca.* 0·5 l., diluted to *ca.* 1 l. with water and extracted five times with 150 ml. petroleum ether to remove the bulk of the chlorophyll. The very bitter-tasting aqueous-alcoholic solution was then shaken out seven times with 100 ml. portions of chloroform, when the aqueous layer was a clear orange colour and was no longer bitter. The combined chloroform extracts were shaken out once with a little water and the chloroform then removed as far as possible, finally *in vacuo* at 70°, to yield *ca.* 300 ml. of a thick green syrup.

The geigerin was extracted from this syrup by stirring with 500 ml. water for 1 h. at 90°, decanting the aqueous layer and, after treating it with animal charcoal at 90° for 15 min., filtering through a bed of silica gel. On refrigerating the yellowish solution after innoculation with geigerin crystals, 3·76 g. of a crystalline mass separated. After repeating this extraction with water another four times, 11·1 g. of crude material was obtained in all, melting over the range *ca.* 85-110°. Recrystallization from hot water yielded 6·45 g. geigerin showing the typical melting point behaviour described earlier[1] for the monohydrate, i.e. softening at 90-100°, re-solidifying and

then melting at 188-191°. The yield of geigerin was thus 0·04% on the air-dried plant material. Analytically pure geigerin was obtained by recrystallizing once more from water, once from chloroform+petroleum ether and finally twice from water (charcoal) to a constant sharp melting point of 192° after partial melting at *ca.* 90-100° followed by resolidification.

The product, dried at 30 mm. pressure over $CaCl_2$ at room temperature, was a hydrated form containing about 1 molecule of water of crystallization. Optical rotation:—

$[\alpha]_D^{17}$ -64° ($CHCl_3$, c=1·096); $[\alpha]_D^{19}$ -63° (EtOH, c=1·015); $[\alpha]_D^{14}$ -65° (EtOAc, c=1·030).

Ultra violet absorption in ethanol (Zeiss Opton) (*Fig.* 2,1):—

λ_{max} (mμ/log ϵ) 239/4·19, 310/1·83.

Anhydrous material was obtained by drying for 4 h. at 103°/0·05 mm. whereby a weight loss of 7·4% was observed.

Found: C, 68·18, 68·25; H, 7·61, 7·51;
calcd. for $C_{15}H_{20}O_4$: C, 68·16, ; H, 7·63%.

Lactone titrations were carried out after heating for 3 h. at 57° in ethanolic KOH solution.

Found: eq. wt. 257, 253;
calcd. for $C_{15}H_{20}O_4$: eq. wt. 264.
(1 lactone group)

Acetylatable hydroxyl groups were determined according to the method of Petersen, Hedberg and Christensen[8], allowing the reaction to proceed for 1 h. at room temperature.

Found: OH, 6·05, 6·55;
calcd. for $C_{15}H_{20}O_4$: OH, 6·44%.
(1 OH)

The infra red spectrum was taken using a film on rock salt and showed a strong absorption band at 2·83 μ, indicating the presence of a hydroxyl group (*Fig.* 1). An acetylation catalyzed by perchloric acid[9] on a 150 mg. sample of geigerin yielded only a brown amorphous product.

Catalytic hydrogenation and dehydrogenation of geigerin

Hydrogenation: Adams' platinic oxide ((100 mg.) in 30 ml. butanol was reduced in hydrogen. Geigerin (1·018 g. hydrated form) and 20 ml. glacial acetic acid were added and the hydrogenation continued until 2 moles of hydrogen had been taken up and absorption had practically ceased. After filtration and drying *in vacuo* at 50°, 1·064 g. of a colourless syrup was obtained in which small needles gradually crystallized. Consecutive crystallizations from ethyl acetate+petroleum ether+methanol, chloroform+benzene, methanol+petroleum ether and ethanol+water (2x) finally gave 96 mg. colourless needles melting over an approximately constant range at 183-198° and depressing the m.p. of a mixture with geigerin to *ca.* 150-160°. For analysis one sample was dried for 5 h. at 100°/0·03 mm. while another sample was sublimed at 160°/0·05 mm.

Found: C, 67·46, 67·50; H, 8·96, 9·02;
calcd. for $C_{15}H_{22}O_4$: C, 67·64 ; H, 8·33;
calcd. for $C_{15}H_{24}O_4$: C, 67·14 ; H, 9·02%.

Ultra violet absorption (Zeiss Opton) in ethanol: broad low maximum at *ca.* 282 mμ, log ϵ 1·07 (*Fig.* 2,2). Both according to the analytical results and the ultra violet absorption, this crystalline product thus still contained ketonic material.

The mother liquors of the above crystallizations were combined and dried *in vacuo* (758 mg. partly crystalline residue) before dehydrogenation.

Dehydrogenation over Pd/C: After initial trials had shown that the yield of azulene dropped on continuing the dehydrogenation for too long, the following procedure was finally used. The crude hydrogenated material (361 mg.) was heated together with 180 mg. palladium on charcoal (10% Pd) under reflux in an atmosphere of carbon dioxide at 280° (metal bath) for 40 min.; evolved gas was collected in a nitrometer over potash solution. Water droplets refluxed while a deep blue condensate appeared within a few minutes.

The gas collected (29 ml. at ambient conditions) was transferred to a specially designed gasometer which permitted of its controlled introduction into the combustion train of a semi-micro combustion unit[10] just ahead of the scavenging tube containing soda-asbestos and anhydrone. Combustion of most of this gas sample yielded 15·92 mg. water and 1·26 mg. carbon dioxide, corresponding to a molar ratio of H_2O : CO_2 of 31 : 1, i.e. equivalent to 3 mole per cent of methane in hydrogen.

The broken-up reaction mass was transferred on to a small filter bed of alumina and washed alternately with ether and methanol until the filtrate was colourless. After drying the filtrate *in vacuo* at 60°, 260 mg. brown syrupy residue was obtained. This was taken up in 2 ml. of benzene, 10 ml. light petroleum ether added and the suspension adsorbed on 15 g. of alumina (Merck, acc. to Brockmann) and eluted with benzene+petroleum ether (9+1). A pure blue frontal zone developed and was eluted with 25 ml. solvent together with following brown material. The product (52 mg. green syrup) was adsorbed on a fresh column of alumina (6 g.) and eluted with petroleum ether only. A single pure blue zone was eluted with 10 ml. solvent and on drying *in vacuo* at 50° yielded 37 mg. of an intense deep blue oil (azulene A).

A trinitrobenzene adduct was obtained from this oil with 32 mg. reagent as 34 mg. small violet-black needles, m.p. 126-130°, which after four crystallizations from 0·4 ml. portions of ethanol yielded 14 mg. adduct, m.p. 133·5-135°.

Found*: C, 60·67, 60·64; H, 5·31, 5·02;
calcd. for $C_{20}H_{19}O_6N_3$: C, 60·46; H, 4·82%.

The m.p. of a mixture with the authentic trinitrobenzene adduct of chamazulene, m.p. 130-131°, was 130-131°. The ultra violet absorption (Zeiss Opton) of the azulene itself (*Fig.* 3,1) was obtained in spectroscopic ligroin followed the method of Pfau and Plattner[11]: λ_{max}(mμ/log ϵ) 245/4·30, 287/4·59, 305/3·96 (infl.), 350/3·57, 370/3·42.

$LiAlH_4$ reduction and dehydrogenation of geigerin

Reduction: A solution of 1·008 g. of anhydrous geigerin in 150 ml. of anhydrous ether+benzene (1+1) was added during 10 min. while stirring to 2·5 g. of $LiAlH_4$ in 60 ml. anhydrous ether and the resultant suspension stirred under reflux for 1 h. The reaction mixture was decomposed with crushed ice followed by 70 ml. 5N HCl, whereby the aqueous layer acquired a cherry red colour. The upper layer was washed twice with a little dilute HCl and a little water, dried, filtered and evaporated to yield a *less reduced product* (*a*) as a semi-solid brown mass (335 mg.). The combined aqueous solutions were then extracted ten times with 20 ml. portions of ether and the ether extract worked up to yield a *more reduced product* (*b*) as a brown resin (442 mg.).

*The trinitrobenzene adducts obtained in this study were not easy to combust without initial conflagration. It appeared, however, that carbon values were steady, while hydrogen values were subject to some fluctuation.

Dehydrogenation over Pd/C

Reduced product (*a*): Exactly following the procedure described above, the reduced product (a) (335 mg.) was dehydrogenated in the presence of 174 mg. Pd/C (10% Pd) for 30 min. at 250°, followed by 60 min. at 280°; 23 ml. (ambient conditions) of gas were collected in the nitrometer. This gas on analysis yielded an equivalent methane content of 8 mole per cent. The crude dehydrogenated product was obtained as a dark brown sticky mass (281 mg.) which was adsorbed on 15 g. alumina (Merck) and eluted with 25 ml. petroleum ether+benzene (4+1) to yield 114 mg. of a brown residue. This was adsorbed on 10 g. alumina (Merck) and eluted with petroleum ether only, when the frontal blue zone first formed separated into two blue bands, the upper band being darker in colour. Both bands were washed out together with 25 ml. of solvent to yield 91 mg. of a dark blue residue. This material was adsorbed again on 20 g. of alumina (BDH) and eluted with petroleum ether only, when a clear separation between the two bands was obtained.

The lower band was eluted and yielded 33 mg. of a pure blue oil (azulene B); addition to 31 mg. symm. trinitrobenzene yielded 21 mg. small violet-brown needles, m.p. 129-133°, which gave 14 mg. adduct melting at 135-137° after two further crystallizations from ethanol. The m.p. of a mixture with the similar adduct from azulene (A) was depressed to 122-123·5°, while the m.p. of a mixture with the authentic trinitrobenzene adduct of chamazulene, m.p. 130-131°, was depressed to 121-123°. Analytical results on this adduct were too variable to allow conclusions as to its composition. The ultra violet absorption of the free azulene in spectroscopic ligroin (*Fig.* 3,2) was obtained (Zeiss Opton) as before, log ϵ being calculated on an assumed composition $C_{14}H_{16}$ for the azulene: λ_{max} (mμ/log ϵ) 245/4·34, 287/4·61, 305/3·99 (infl.), 250/3·62, 370/3·37.

The upper and darker blue band was eluted separately and yielded 24 mg. of a royal blue oil (azulene C). Reaction with 17 mg. trinitrobenzene yielded 14 mg. small violet-black needles giving 12 mg. adduct, m.p. 154-158° after one crystallization from ethanol. This was combined with the similar product obtained below.

Reduced product (*b*). The product (442 mg.) was dehydrogenated as above with 220 mg. Pd/C (10% Pd) for 75 min. at 280°. The gas evolved (34 ml. at ambient conditions) on analysis yielded an equivalent methane concentration of 30 mole per cent. The reaction product was isolated as before (357 mg. brown residue) and adsorbed on 20 g. of alumina (BDH). Elution with 60 ml. of petroleum ether+benzene (4+1) yielded 79 mg. green syrup which was re-adsorbed on 30 g. alumina (BDH) when elution, with petroleum ether only, achieved resolution into two deep blue bands as before.

The lower band was eluted alone and the product, 30 mg. pure blue oil (azulene B), converted to the trinitrobenzene adduct (22 mg. product with 20 mg. reagent yielding 26 mg. adduct), which after two crystallizations from ethanol gave 14 mg. of violet-black needles, m.p. 134-137°. No depression of the m.p. occurred in a mixture with the similar adduct obtained from azulene (B) above.

The upper and darker blue band was eluted and yielded 10 mg. deep blue residue (azulene C) which with 10 mg. reagent yielded 12 mg. violet-black needles of trinitrobenzene adduct. One crystallization from ethanol yielded 9 mg. adduct, m.p. 156-160°, which was combined with 12 mg. adduct obtained from azulene (C) in the foregoing dehydrogenation. One crystallization from ethanol then yielded 16 mg. adduct, m.p. 159-160°.

Found: C, 61·20; H, 4·56;
calcd. for $C_{21}H_{21}O_6N_3$: C, 61·30; H, 5·15%.

The ultra violet absorption (*Fig.* 3,3) was measured (Zeiss Opton) in spectroscopic

ligroin as before: λ_{max} (mμ/log ϵ) 252/4·25, 295/4·53, 320/4·10 (infl.), 360/3·69, 375/3·65 (shoulder), 390/3·50.

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PROPERTIES OF THE BORON HALIDES

PART VI—THE VISCOSITY OF BORON TRICHLORIDE IN THE RANGE 30°C TO 230°C

by

J. HAWES,* H. A. E. MACKENZIE,* and C. J. G. RAW

OPSOMMING

Die viskositeit van boortrichloried is tussen 30°C en 230°C bepaal. Die Sutherlandse konstante is eers afhanklik van die temperatuur, maar dit bly 'n konstante (C=389°K) by die temperature bo 120°C.

SUMMARY

The viscosity of boron trichloride has been determined between 30°C and 230°C. The Sutherland constant is at first dependent on the temperature, but it remains constant (C=389°K) at the temperatures above 120°C.

EXPERIMENTAL

The apparatus is schematized in *Fig.* 1. In essentials the method consisted in distilling boron trichloride from a "supplier bulb" (A in *Fig.* 1), surrounded by an ice-water mixture, to a "receiver bulb" (B in *Fig.* 1), surrounded by a dry ice-ethanol freezing mixture, *via* a preheater helix of glass tubing and a short length of capillary tubing (C in *Fig.* 1), both of which were immersed in a thermostat. The boron trichloride was prepared from boron trifluoride by passing the boron trifluoride over aluminium chloride at a temperature of about 200°C. The resulting boron trichloride was trapped out in a dry ice-ethanol trap, and later purified by vacuum distillation to a constant vapour pressure of 483 mm. at 0°C.

This boron trichloride was then introduced by vacuum distillation into the "supplier bulb" (A in *Fig.* 1). Its vapour pressure at 0°C was once more checked, and a determination was then made at a selected thermostat temperature. The thermostat, a stainless steel Dewar vacuum flask containing a high boiling point oil for use at higher temperatures or water for use at lower temperatures, was electrically heated and stirred. A mercury-toluene thermoregulator and an electronic relay ensured that the thermostat temperature varied by less than 0·1°C, except at the highest temperatures where the maximum variation was about 0·2°C.

During each determination, of about forty minutes duration, the pressures of the receiver and supplier bulbs were noted every five minutes, and were found to remain essentially constant. These pressures were noted, and where small variations did occur, the two pressures were averaged.

Both "supplier" and "receiver" bulbs were weighed empty, and A (in *Fig.* 1), was reweighed after the introduction of the boron trichloride. After a run had been completed, each bulb was reweighed so that the weight of boron trichloride transferred per unit time could be obtained. While weighing the bulbs containing boron trichloride, the stopcocks were spring-loaded with stout rubber bands. (During the winter, when the measurements were made, the room temperature at which the bulbs were weighed was usually between two and ten degrees above the boiling point of boron trichloride.)

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Essential dimensions of the viscometer are as follows:

Length of capillary tube=4·173 cms. (measured at room temperature using a travelling microscope). Internal radius of the capillary tube=0·05047 mm. (measured at room temperature from the weight and length of a mercury thread).

The usual theory[1] for a transpiration method of determining the viscosity of a gas could be applied, and the equation used to calculate the viscosity coefficient (η) was

$$\eta = \frac{M\pi r^4}{w} \cdot \frac{(p_1 - p_2)}{8lRT} \cdot \frac{(p_1 + p_2)}{2},$$

where M is the molecular weight (117·20 for boron trichloride), r is the internal radius of the capillary tube, l is the length of the capillary tube, p_1 and p_2 are the pressures at the supplier and receiver bulbs respectively, T is the absolute temperature, w is the weight of boron trichloride transferred per unit time, and R is the molar gas constant.

RESULTS AND DISCUSSION

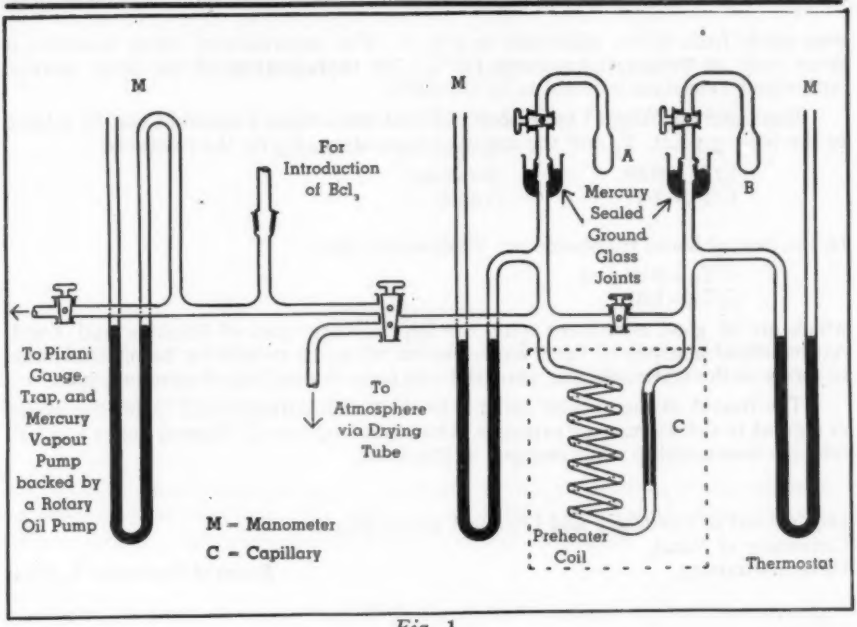
The results obtained for the viscosity of boron trichloride are listed in the following table:

Temperature, T (°K)	$10^7\eta$ (in g.cm.$^{-1}$sec.$^{-1}$	$T^{3/2}/10^7\eta$
303·2	1223	4·32
	1219	4·33
333·2	1326	4·70
	1330	4·68
	1325	4·70
370·5	1398	5·10
	1402	5·09
393·2	1474	5·29
	1479	5·27
	1477	5·28
410	1536	5·40
	1541	5·39
438·6	1638	5·61
	1646	5·58
451·7	1699	5·65
	1689	5·68
473·2	1769	5·82
	1768	5·82
505·2	1880	6·04
	1878	6·05
	1884	6·03

The error in a result was estimated to be $\pm 8\times10^{-7}$ g.cm.$^{-1}$ sec.$^{-1}$ Sutherland's equation for the variation of the viscosity of a gas with temperature can be writteu in the form[1]:

$$T = \frac{KT^{3/2}}{\eta} - C$$

where K and C are constants. C is the Sutherland constant, and can be obtained as the negative intercept on the T-axis if T is plotted against $T^{3/2}/\eta$. This plot has


M
M
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For
Introduction
of BCl3
A
B
Mercury
Sealed
Ground
Glass
Joints
To Pirani
Gauge,
Trap, and
Mercury
Vapour
Pump
backed by
a Rotary
Oil Pump
To
Atmosphere
via Drying
Tube
C
M – Manometer
C – Capillary
Preheater
Coil
Thermostat

Fig. 1.

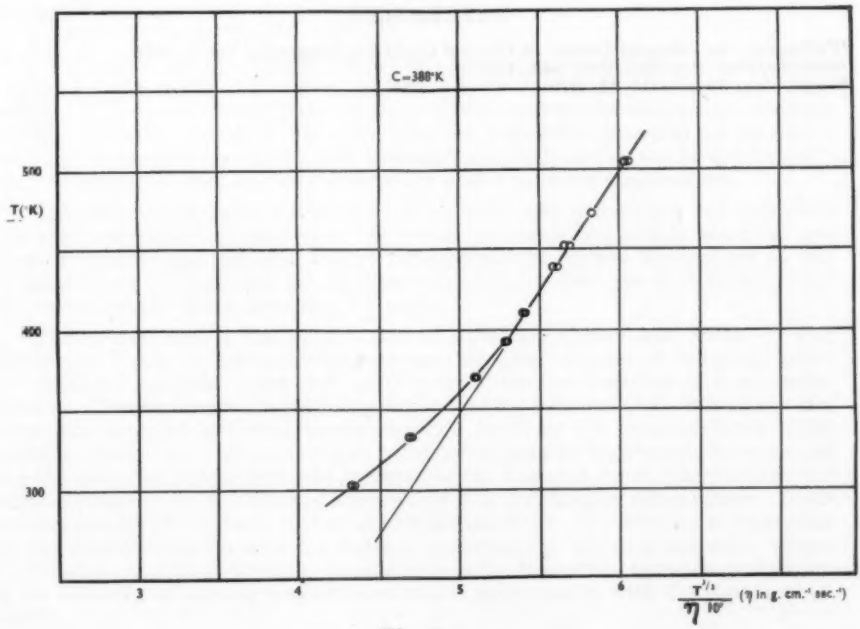
C=388°K
500
T(°K)
400
300
3
4
5
6
T^1/2 / η 10^7 (η in g. cm.^-1 sec.^-1)

Fig. 2.

been made from boron trichloride in *Fig.* 2. The experimental curve, however, is linear only at temperatures above 120°C. By extrapolation of the linear portion Sutherland's constant is found to be C=389°K.

Rankine[2] and Vogel[3] have observed that Sutherland's constant can be related to the boiling point, T_b and the critical temperature, T_c, by the relations:

$C/T_c = 0{\cdot}89$ (Rankine).
$C/T_b = 1{\cdot}47$ (Vogel).

In the case of boron trichloride our experiments give:

$C/T_c = 0{\cdot}86$ and
$C/T_b = 1{\cdot}37$,

which are in good agreement with the approximate rules of Rankine and Vogel. A theoretical analysis of these experimental viscosity results for boron trichloride in terms of the intermolecular potential will form the subject of another paper.

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PROPERTIES OF THE BORON HALIDES

PART VII—THE INTERMOLECULAR POTENTIAL OF BORON TRICHLORIDE

by

C. J. G. RAW

OPSOMMING

Die Lennard-Jones intermolekulêre kragkonstantes van boortrichloried is uit eksperimentele viskositeitsgegewens bereken. Die waardes is: $\epsilon/k = 346°K$ en $r_o = 5{\cdot}10$Å. Hierdie konstantes is gebruik om sekere ander eienskappe van boortrichloried te bereken.

SUMMARY

The Lennard-Jones intermolecular force constants of boron trichloride have been calculated from experimental viscosity data. The values are: $\epsilon/k = 346°K$ and $r_o = 5{\cdot}10$Å. These constants have been used to calculate certain other properties of boron trichloride.

One of the most convenient and, at the same time, realistic ways of representing the interaction energy of two non-polar molecules is the Lennard-Jones (12,6) potential[1]:

$$E(r) = 4\epsilon[(r_o/r)^{12} - (r_o/r)^6],$$

where E(r) is the energy of interaction of two molecules whose centres are a distance r apart, ϵ is the depth of the potential well (i.e. the maximum energy of attraction between the two molecules), and r is the collision diameter for low-energy collisions (i.e. the value of r for which $E(r)=0$). The two adjustable potential parameters, ϵ (or, more commonly, ϵ/k where k is Boltzmann's constant) and r_0, can be determined[1] from experimental data on the gas viscosity over a range of temperatures.

The viscosity of boron trichloride has recently been determined and published in a previous paper[2] in this series. As boron trichloride is a simple non-polar gas whose intermolecular potential energy function should be well represented by the Lennard-Jones (12,6) model, the experimental viscosity data was used to determine the intermolecular force constants, ϵ/k and r_0.

The method used in this work is that of Hirschfelder, Bird, and Spotz[3,4]. The viscosity of non-polar gases can be expressed in terms of a set of integrals, called the "collision integrals" since they involve explicitly the dynamics of a molecular collision. These collision integrals thus depend on the intermolecular force law. If a particular empirical potential energy function (such as the Lennard-Jones (12,6) model) is chosen, the collision integrals become functions of the absolute temperature and the potential parameters. In the case of the Lennard-Jones (12,6) model, the collision integrals are functions of kT/ϵ, where T is the absolute temperature. These collision integrals have been evaluated and tabulated[1,3]. The theoretical expression for the viscosity also involves the collision diameter, r_0. By trial and error, values of ϵ/k and r_0 are chosen which on substitution in the theoretical equation give values of the viscosity at various temperatures which agree exactly with the experimental results.

Some simple approximate relations exist which enable a rough estimate of ϵ/k to be made from a knowledge of certain properties of the gas. This greatly simplifies the trial and error process mentioned above. Two such relations[4] from the Lennard-Jones and Devonshire theory of liquids and gases are:

$$\epsilon/k \sim 0{\cdot}75T_c$$
$$\epsilon/k \sim 1{\cdot}39T_b$$

where T_c is the critical temperature, and T_b is the boiling point. Another such relation, due to the author[5], is:

$$\epsilon/k \sim 0{\cdot}88C$$

where C is Sutherland's constant (from the temperature dependence of the gas viscosity). This last approximation is especially useful since ϵ/k can be obtained roughly from the very data from which it is later computed exactly.

For boron trichloride, $\epsilon/k \sim 339°K$ (from the critical temperature), $\epsilon/k \sim 342°K$ (from Sutherland's constant), and $\epsilon/k \sim 397°K$ (from the boiling point).

The exact values of the potential parameters, determined by trial and error, are $\epsilon/k = 346°K$ and $r_0 = 5{\cdot}10Å$.

The following table shows a comparison between experimental[2] and calculated values of the viscosity (in g.cm.$^{-1}$sec.$^{-1}$) at various temperatures.

T(°K)	kT/ϵ	$10^7\eta$(calc.)	$10^7\eta$ (exp.)
370·5	1·071	1393	1398
393·2	1·136	1477	1477
410	1·185	1539	1536
438·6	1·268	1644	1646
451·7	1·305	1690	1689
473·2	1·368	1769	1769
505·2	1·460	1878	1880

The values of ϵ/k from the critical temperature and Sutherland's constant are in particularly good agreement with the accurate value, and in the case of the boiling point the agreement, while not quite as good, is still satisfactory. From data on "atomic radii"[6], boron has a "radius" of 0·88 Å, and chlorine one of 0·99 Å, which gives a maximum "diameter" of 5·72 Å to the boron trichloride molecule. This is in good agreement with the value of the collision diameter of boron trichloride ($r_0 = 5{\cdot}10Å$).

These intermolecular force constants can be used to calculate a wide variety of other physical properties of gases and liquids[1]. As examples, the critical volume[4], the parachor[1], and the activation energy for viscous flow[7], assuming that boron trichloride forms a normal liquid, can be predicted. The relations to be used are:

$$r_0 \sim (8{\cdot}33 \times 10^7)(V_c)$$
$$P \sim (7{\cdot}1 \times 10^{23})\epsilon^{1/4} r_0^{5/2}$$
$$\Delta E_{vis} \sim 4{\cdot}5\ \epsilon/k \text{ cals. mole}^{-1}$$

where V_c is the critical volume; ϵ/k and r_0 are the Lennard-Jones parameters; P is the parachor, and ΔE_{vis} is the activation energy for viscous flow.

For boron trichloride, these relations give $V_c \sim 1{\cdot}266$ cm.^{3}g.$^{-1}$; $\Delta E_{vis} \sim 1577$ cals. mole^{-1}; and $P = 195{\cdot}0$.

As the intermolecular force constants of both boron trifluoride[8] and boron trichloride are now known, it is possible to calculate the mutual interaction energy of the molecules of the two different gases. Experimental evidence in confirmation of this interaction potential should be obtained from an investigation of inter-diffusion and thermal diffusion in gaseous boron trifluoride-boron trichloride mixtures.

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THE SPECTROGRAPHIC ANALYSIS OF TRACE ELEMENTS IN PLANT MATERIALS

A COMPARISON BETWEEN THE ANODE ARC AND CATHODE LAYER ARC METHODS OF EXCITATION

by

A. STRASHEIM and L. CAMERER*

OPSOMMING

'n Vergelykende studie is gemaak van die geskiktheid van die anode en katode opwekkings metodes vir die spektrochemiese ontleding van spoorelement-oksiedekstrakte gekonsentreer volgens die Mitchell metode.

Die volgende algemene gevoltrekkings is gemaak:

(1) Die noukeurigheid van die twee verskillende metodes is omtrent dieselfde.
(2) Die inlynstelling van die anode-boog is minder krities as die van die katode-boog.
(3) Die elemente kobalt en molibdeen kan beter met behulp van die katode- as die anode-boog bepaal word.

Vir die ontleding van spoorelement-oksiedekstratke word die katode- dus bo die anode-boog verkies.

SUMMARY

A comparison is made between the relative merits of the cathode and anode methods of excitation when trace element oxide concentrates are analysed spectrochemically.

The following conclusions are reached:

(1) The accuracies obtainable by the two methods of excitation are about the same.
(2) The alignment of the anode arc is less critical than that of the cathode.
(3) The cathode method appears to be the more suitable for the determination of cobalt and molybdenum.

INTRODUCTION

Elements of nutritional importance in plant ash and soil extract solutions can economically be determined spectrochemically[1] when

(i) potassium, sodium and calcium are determined flame photometrically;
(ii) magnesium, copper, barium, strontium, manganese, aluminium and iron are determined directly on the ash;
(iii) nickel, cobalt, molybdenum, tin, lead, titanium, vanadium, chromium, *etc.* are first concentrated with organic reagents and then analysed spectrographically.

The important elements phosphorus and boron are not included in this list. Phosphorus is usually determined colorimetrically and boron by a spectrochemical technique specially developed for this purpose.

This paper concerns the spectrographic determination of the trace elements nickel, cobalt, molybdenum, *etc.*

With minor variations, the chemical concentration method developed by Mitchell[2] has proved satisfactory in a number of laboratories[3]. The spectrographic procedure, however, differs in different laboratories. Mitchell used a cathode excitation, whereas Heggen and Strock[3] use an anode excitation.

Until quite recently anode excitation was generally preferred in this laboratory. The sensitivity of this method was, however, found to be inadequate for the very low cobalt concentrations which occur in some South African plant materials. It was accordingly decided to investigate the relative merits of anode and cathode excitation when the final precipitates of the Mitchell trace element concentration procedure are analysed spectrochemically.

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APPARATUS

Excitation Source: A 230 volt direct current arc source.

Spectrograph: Hilger large quartz and glass spectrograph. Quartz optics are used and the spectrum from 4700A to 2750A is photographed on a 10 inch plate.

Microphotometer: "Zeiss Spektrallinien-Photometer."

Developing Equipment: A.R.L. developing and plate drying machines.

Calculating Equipment: A.R.L. calculating board fitted with Seidel scales.

Arc Stand and Optical Systems: A water-cooled electrode holder[4] is used. A 1 : 1 image of the arc is first focussed on a 4 mm. diaphragm. This diaphragm is then focussed in the collimator of the spectrograph with 6x enlargement. For routine alignment of the arc in the optical path of the condenser system of the spectrograph, two 2x and 30x images are projected on suitable screens. Scales are engraved on these screens and aligned with the diaphragm opening, taking the centre of the diaphragm as origin.

PROCEDURE

Excitation and recording conditions

Excitation and recording conditions of the cathode and anode arcs are summarised below.

	ANODE	CATHODE
Excitation:	The samples are arced in triplicate at a current of 13 amp. short-circuited.	The samples are arced in triplicate at a current of 9 amp.
Exposure:	± 2 min.	± 3 min.
Sector:	4 steps; 100%, 50%, 25%, 12½%.	
Electrode System:	The lower sample-carrying electrode (anode) is a high-purity graphite rod, 0·25 inches in diameter, with a cup 8 mm. deep, an inner diameter of 1 mm. and an outer diameter of 2·9 mm. cut down to 12 mm. The upper electrode (cathode) is a pure carbon rod with a diameter of 5 mm., cut round at the top.	The lower sample-carrying electrode (cathode) is a pure carbon rod 5 mm. in diameter, with a cup having the same dimensions as that of the anode arc. The upper carbon electrode dimensions are similar to that of the anode arc.
Electrode separation:	9 mm. The central 4 mm. portion of arc is photographed.	9 mm. The cathode layer and 4 mm. of arc measured from the cathode are photographed.
Plates:	Ilford Thin Film Half Tone	
Plate processing:	Developed in 1 : 1 I.D.13 for 6¼ min. at 18°C and fixed for 1 min. in a fixer consisting of 400 g. sodium thiosulphate and 20 g. sodium bisulphite made up to 1 l.	

Photometry

The transmittance of the analytical and internal standard line pairs listed below are determined and converted to relative intensities, using an emulsion calibration curve established according to the two-line method of Churchill[6].

Analytical line pairs

ELEMENT	LINE PAIR
Chromium	Cr 4254/Fe 4236
Cobalt	Co 3454/Fe 3413
Nickel	Ni 3414/Fe 3413
Zinc	Zn 3345/Fe 3306
	Zn 3345/Cd 3261
Titanium	Ti 3242/Fe 3244
Vanadium	V 3185/Fe 3197
Tin	Sn 3175/Fe 3197
Molybdenum	Mo 3170/Fe 3197
Lead	Pb 2833/Fe 2838
	Pb 2833/Cd 3261

Sample preparation and excitation

(i) *General concentration procedure:*

The 8 oxy-quinoline, tannic acid and thionalide mixed reagent concentration procedure described by Mitchell and Scott[2] proved very satisfactory. Mitchell and Scott used iron as a variable internal standard, but, as the present authors wished to use only one analysis curve per analytic element, Mitchell and Scott's procedure had to be changed somewhat. When iron is used as an internal standard in plant analyses, the iron present in the analytic solutions should have a higher concentration than that usually found in plant materials. The colorimetric method described by Scott[5] for determining the amount of iron present in the extracted analytical solutions was found to be unreliable because of variable phosphate concentrations. The orthophenanthroline method[1,9] was found to be satisfactory.

About 20 g. of ground oven-dried plant material in a loosely covered silica basin are ashed overnight at 450°C in an electric muffle furnace through which a slight draught of air is drawn. The ash is then transferred to a platinum crucible, mixed with 4 g. sodium carbonate, and fused. The melt is extracted with hot hydrochloric acid and water. After taking the sample to dryness to dehydrate the silica, 50 ml. 6N hydrochloric acid is added and gently boiled for at least 15 min. to hydrolise all pyrophosphate to orthophosphate. Sufficient water is added to dissolve all the soluble salts, the silica is filtered off and the filtrate made up to 100 ml. after washing the silica precipitate with small quantities of boiling water. An aliquot of the sample solution containing 0·04-0·2 mg. Fe_2O_3 (generally 1 or 2 ml. of the solution) is taken for the iron determination. (The final analytical result is corrected for this aliquot taken from the solution sample for the iron determination.)

When the iron content of the solution sample is known, iron is added until the sample contains 10 mg. Fe_2O_3. If the solution sample contains more than 10 mg. Fe_2O_3 an aliquot containing 10 mg. Fe_2O_3 is taken. The solution is then transferred to a 400 ml. Phillips beaker and diluted to about 150 ml. To the sample is added Al_2O_3 in the form of $AlCl_3$ solution. It is desirable to have about 30 mg. Al_2O_3 as co-precipitant in the sample solution. The amount of Al_2O_3 that has to be added is usually known from the direct analyses made on

the ash. In addition to the Al_2O_3 1 ml. cadmium solution, containing ·588 mg. cadmium, is added. The further concentration procedure closely resembles that of Scott and Mitchell[2]. The final pH of the solution is, however, critically controlled with Merck's special indicator paper. The final precipitate after ashing is allowed to reach moisture equilibrium, weighed (usually between 50 and 60 mg.) and ground together with an equal weight of National Carbon SP2 grade graphite powder in an agate mortar. This mixture is stiffly packed into the cups of the sample-bearing electrodes.

(ii) *Preparation of Standards:*

To avoid the precipitation procedure, standards resembling the composition of the final ashed precipitates were tried. These were found to be unsatisfactory and synthetic plant ash standards according to Farmer's[7] specification were prepared. The dilutions of the trace elements were made in steps in a ratio of 1 : 0·316 as suggested by Mitchell[8]. The range of the trace element concentrations varied for chromium, cobalt, nickel, vanadium, tin, molybdenum and lead from 300 p.p.m. to 0·1 p.p.m., for zinc from 3000 p.p.m. to 1 p.p.m. and for titanium from 600 p.p.m. to 0·2 p.p.m. Two sets of ashed precipitates were prepared and stored in vials with plastic caps.

(iii) *Excitation:*

(a) Anode arc: To avoid sputtering of the sample material, the samples are preheated for a few seconds at 1·2 amp. before striking the arc. The current and arc gap are then simultaneously increased to about 11 amp. (exactly 13 amp. short-circuited) and 9 mm. respectively. The sample is burnt to completion, adding 20 sec. for the complete volatilization as suggested by Heggen and Strock[3]. During the arcing period the arc gap is maintained at 9 mm., while the central 4 mm. portion of the arc is being photographed. The total excitation time varies from 100 to 120 sec.

(b) Cathode arc: A preliminary experiment showed the "best setting" of the image of the cathode to be between 1 and 2 mm. below the centre of the diaphragm. Using the 30x enlarged screen a further six exposures were photographed setting the visible image of the cathode at 1, 1·2, ... 1·8 and 2 mm. below the centre of the diaphragm. This experiment was repeated three times. After measuring the blackening of the analysis and corresponding internal standard lines, the relevant intensity ratios were calculated and plotted against the different positions of the cathode (*Fig.* 1.).

From the results illustrated in *Fig.* 1 it can be concluded that the intensity ratios of the elements chromium, cobalt, lead, molybdenum, vanadium and tin do not vary appreciably when the cathode is shifted by 1 to 2 mm. from the centre of the diaphragm, that the intensity ratio of nickel decreases when the cathode is moved towards the centre of the diaphragm, and that the zinc/cadmium intensity ratio is less dependent on the position of the cathode than the zinc/iron ratio. The intensity ratio zinc/cadmium is thus to be preferred for the analysis of zinc. It is also evident that the titanium/iron intensity ratio depends strongly on the position of the cathode.

Generally it can be concluded that for satisfactory zinc, nickel and titanium analyses, the position of the image of the cathode on the diaphragm must be critically controlled.

As "best setting" of the cathode image, a setting of 1·4 mm. from the centre of the diaphragm was chosen, this position showing the least scatter. (See *Fig.* 1).

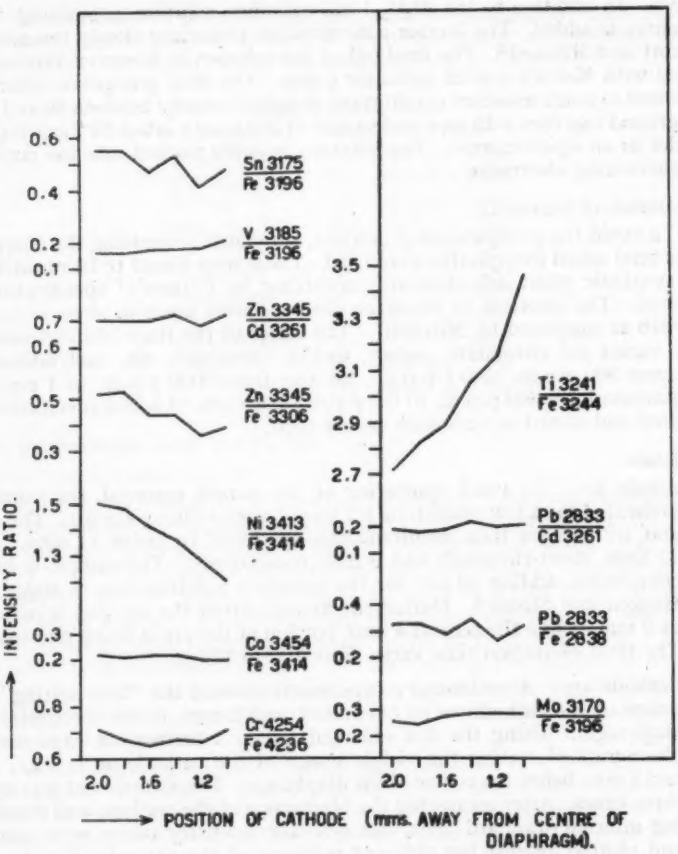
Sn 3175 / Fe 3196
V 3185 / Fe 3196
Zn 3345 / Cd 3261
Zn 3345 / Fe 3306
Ni 3413 / Fe 3414
Co 3454 / Fe 3414
Cr 4254 / Fe 4236
Ti 3241 / Fe 3244
Pb 2833 / Cd 3261
Pb 2833 / Fe 2838
Mo 3170 / Fe 3196
INTENSITY RATIO.
POSITION OF CATHODE (mms. AWAY FROM CENTRE OF DIAPHRAGM).

Fig. 1.—The dependence of intensity ratio on cathode position.

(iv) *Analysis curves:*

Using the two sets of final precipitates, prepared as described above, two series of analysis curves with anode and cathode excitation were made. The curves for zinc and nickel are illustrated in *Fig.* 2 and 3.

(v) *Comparison between anode and cathode arc excitation:*

From the analysis curves, conclusions can be drawn regarding the following

(a) Sensitivity.

(b) Influence of background on the analysis curve: If the analytic element is absent in the blank spectrum the asymptotic slope of the curve towards the x-axis is an indication of the effect of the background on the intensity ratios of the analysis and internal standard lines.

(c) Accuracy: The slopes of the analysis curves give an indication of the accuracy of analysis, seeing that the same spectrograph, microphotometer, standards, etc. were used.

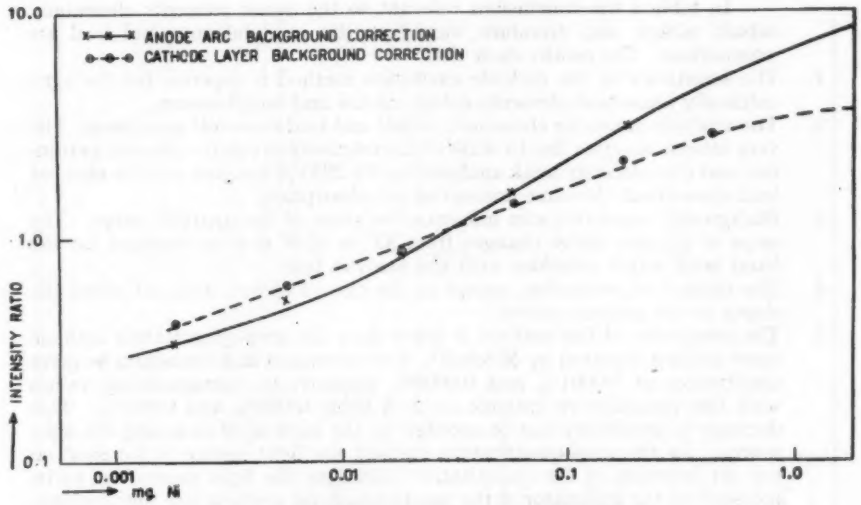

Fig. 2.—Working curve for Ni 3414/Fe 3413.

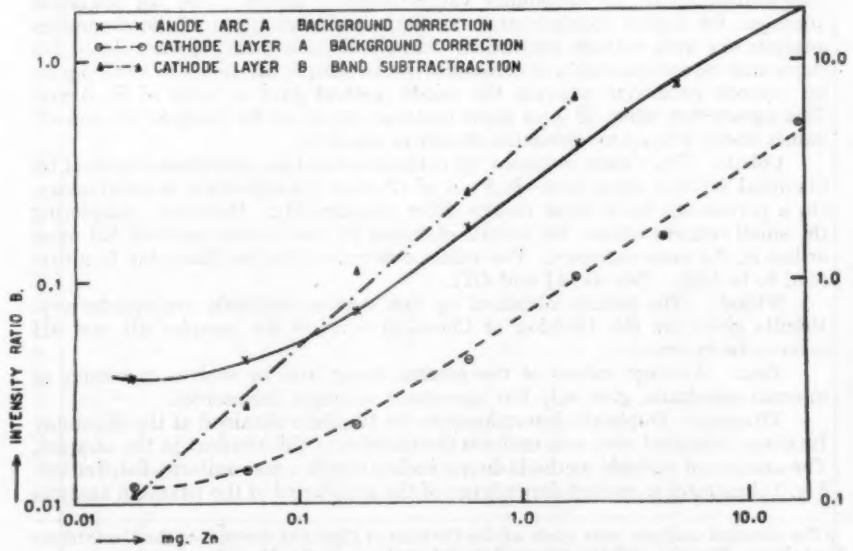

Fig. 3.—Working curve for Zn 3345/Fe 3306.

In table I the conclusions relevant to the minor elements chromium, cobalt, nickel, zinc, titanium, vanadium, tin, molybdenum and lead are summarised. The results show that:

1. The sensitivity of the cathode excitation method is superior for the agriculturally important elements cobalt, nickel and molybdenum.
2. The analysis curves for chromium, nickel and lead show self-absorption. The very intense analysis line Cr 4254 of the relatively involatile element chromium and the relatively weak analysis line Pb 2833 of the very volatile element lead show about the same amount of self-absorption.
3. Background correction can influence the slope of the analysis curve. The slope of the zinc curve changes from 32° to 42·5° if it is corrected for the band head which coincides with the analysis line.
4. The method of excitation, except in the case of nickel, does not affect the slopes of the analysis curves.
5. The sensitivity of this method is lower than the semi-quantitative cathode layer method reported by Mitchell[9]. For chromium and vanadium he gives sensitivities of 0·0001% and 0·0005% respectively, corresponding values with this quantitative cathode method being 0·003% and 0·001%. This decrease in sensitivity can be ascribed to the method of focussing the light source. In the semi-quantitative method the light source is focussed on the slit, whereas in the quantitative technique the light source has to be focussed on the collimator of the spectrograph for uniform line illumination.

(vi) *Application of anode and cathode arc excitation:*

These two methods of excitation have been used for the analysis of certain plant samples. The results, together with those obtained chemically and spectrochemically at two other laboratories*, are tabulated in table II.

From these results the following can be concluded:

Chromium: The cathode and anode methods used in this laboratory give comparable results for chromium values below 4 p.p.m. The big deviation obtained for higher concentrations is due to self-absorption of the chromium analysis line with cathode excitation. Sample 4I (sick tobacco) was diluted ten times and the concentration of chromium in this sample was found to be 43 p.p.m. by cathode excitation whereas the anode method gave a value of 56 p.p.m. This means that when 20 g. of plant material are ashed for analysis all cathode values above 4·5 p.p.m. chromiun should be checked.

Cobalt: The values obtained by cathode excitation and those obtained by Chemical Services agree best—in 8 out of 12 cases the agreement is satisfactory. On a percentage basis these results differ considerably. However, considering the small concentrations, the results obtained by the various method fall more or less in the same category. The values determined by the Macaulay Institute tend to be high: (See 4I, 4J and 4K).

Nickel: The results obtained by the various methods are satisfactory. Results given by the Division of Chemical Services for samples 4B and 4H seem to be in error.

Zinc: Average values of the results, using iron as well as cadmium as internal standards, give only fair agreement amongst themselves.

Titanium: Duplicate determinations for titanium obtained at the Macaulay Institute indicated very non-uniform distribution of this element in the samples. The anode and cathode methods do not indicate such a non-uniform distribution. *Fig.* 1 illustrates a marked dependence of the sensitivity of the titanium analysis

*The chemical analyses were made at the Division of Chemical Services of the Department of Agriculture, Pretoria, and the spectrochemical analyses at the Macaulay Institute for Soil Research, Aberdeen, Scotland.

TABLE I

SENSITIVITY, INFLUENCE OF BACKGROUND AND ACCURACY OF MINOR ELEMENT ANALYSIS.

Element	*Intensity of analysis line	Line pair	†Type of Excitation	Sensitivity in mg.	Influence of background	Accuracy	Remarks
Chromium	5000 R.	Cr 4254 / Fe 4236	A.	·002	Background correction must be made.	Both excitations give curves having a slope of 280°.	Determination of relative intensities difficult due to the steep slope of the Ilford Thin Film Half Tone plate in this wavelength region.
			C.	·022	Background correction must be made.		
Cobalt	3000 R.	Co 3454 / Fe 3413	A.	·006	Even with background correction C-curve shows toe shape for low concentrations.	Anode excitation gives a slope of 39·5°, whereas C excitation gives a 34° slope A—superior.	Values between ·0006 and ·002 mg. can be estimated using C excitation.
			C.	·002			
Nickel	1000 R.	Ni 3414 / Fe 3413	A.	·002	For Ni-values below ·02 mg. A curve shows toe-shape.	A curve slope 30° C curve slope 20° A superior.	Both curves show selfabsorption for Ni concentrations above 4 mg.
			C.	·002	—		
Zinc	800	Zn 3345 / Fe 3506	A.	·2	Background corrected curves show toe shape for low Zn concentrations.	Slope of curve 37·°.	
			C.	·2		Slope of curve 35°.	
		Zn 3345 / Cd 3261	A.	·2	Background corrected curves show toe shape for low Zn concentrations.	Slope of curve 32°.	The zinc analysis line coincides with a band head. If analysis curve is corrected for this band head a curve with a slope of 42·5° is obtained—a slope near that of an ideal analysis curve. Sensivitity is then in the order of ·02 mg.
			C.	·2			
Titanium	60	Ti 3242 / Fe 3244	A.	·01		Same slope—39°	
			C.	·01			
Vanadium	500 R.	V 3185 / Fe 3197	A.	·002	Background evident for very low vanadium values with C excitation.	Slope 35°.	
			C.	·0006		Slope 40°.	
Tin	400	Sn 3175 / Fe 3197	A.	·006		Slope 35°.	
			C.	·006		Slope 35·5°.	
Molybdenum	1000 R. Fe 3197	Mo 3170 / Fe 3187	A.	·006		Slope 39°.	Using C excitation molybdenum can be estimated to ·0006 mg.
			C.	·002		Slope 35°.	
Lead	500 R.	Pb 2833 / Fe 2838	A.	·006		Slope 21°.	
			C.	·006		Slope 27°.	
		Pb 2833 / Cd 3261	A.	·006		Slope 26°.	
			C.	·006		Slope 26°.	

*Intensity of analysis lines given as in M.I.T. wavelength tables.
†A=Anode. C=Cathode.

TABLE II

COMPARISON OF DIFFERENT VALUES (IN P.P.M.) OF TRACE ELEMENTS IN PLANT MATERIAL

The samples have been tested by:

(i) The Macaulay Institute for Soil Research, Aberdeen, with the cathode layer method.
(ii) The Department of Agriculture, Division of Chemical Services, Pretoria, chemically.
(iii) The Spectrochemical Department of the C.S.I.R., Pretoria.

(a) with the anode arc;
(b) with the cathode layer method.

	Cr	Co	Ni	Zn	Ti	V	Sn	Mo	$\frac{Pb}{Fe}$	$\frac{Pb}{Cd}$		Sample
C.S.I.R. Anode	1·3	<0·3	2·4	28	11	0·20	0·6	<0·1	1·7			
C.S.I.R. Cathode	1·2	<0·1	2·2	22	9	0·21	0·1-0·3	~0·04	1·1	1·1	4A	Peach leaves.
Mac. I.		0·15	3·3	21	11-13	0·3	<1·0	0·05	6·5			
Chem. Service		0·1	2·8	26				0·1				
C.S.I.R. Anode	2·0	~0·1	4·8	60	42	0·51	0·51	2·0	3·9	2·7		
C.S.I.R. Cathode	1·8	0·16	6·4	60	32	0·78	0·1-0·3	1·7	2·2	1·5	4B	Bean leaves.
Mac. I.		0·36	6·6	60	40-82	1·0	<1·0	1·7	3·0			
Chem. Service		0·3	0·5	56				3·5				
C.S.I.R. Anode	0·6	0·1-0·3	2·2	22	22	0·40	0·48	0·85	1·4	1·2		
C.S.I.R. Cathode	0·8	0·21	3·3	18	20	0·45	0·3	0·67	1·3	1·1	4C	Garden beet
Mac. I.		0·37	2·0	30	24-39	0·70	<1·0	0·85	6·0			leaves.
Chem. Service		0·1	2·5	23				2·7				
C.S.I.R. Anode	2·3	<0·3	3·0	59	42	0·9	0·31	5·3	4·6			
C.S.I.R. Cathode	2·3	0·15	3·3	39	40	1·0	<0·16	3·9	2·7	4·8	4D	Little gem
Mac. I.		0·33	4·0	60	45-74	1·1	<1·0	3·3	5·5			leaves.
Chem. Service		0·5	3·0	38				5·5				
C.S.I.R. Anode	0·2	0,49	1·5	64	9·3	0·28	0·26	<0·1	1·4	3·0		
C.S.I.R. Cathode	0·2	0·54	2·1	93	7·7	0·13	<0·1	<0·05	~0·5	1·0	4E	Prune tree
Mac. I.		0·76	1·8	52	9-13	0·3	<1·0	0·05	5·5			leaves.
Chem. Service		0·8	·19	30				1·5				
C.S.I.R. Anode	5·4	0·67	5·2	26	27	0·9	1·1	0·84	2·6	4·7		
C.S.I.R. Cathode	3·5	0·58	6·1	21	28	0·9	0·8	0·74	2·7	3·2	4F	Lucerne.
Mac. I.		0·77	5·0	50	39-40	1·0	<1·0	0·87	3·5			
Chem. Service		0·6	6·3	18				1·2				
C.S.I.R. Anode	4·0	0·37	2·5	25	23	0·72	0·53	<0·1	1·6	1·7		
C.S.I.R. Cathode	3·3	0·35	4·5	28	31	0·68	0·3	<0·03	~0·9	~0·5	4G	Bush.
Mac. I.		0·63	4·1	26	22-30	0·7	1·05	8·0				
Chem. Service		0·3	6·5	41				1·5				
C.S.I.R. Anode	15·2	0·88	9·9	28	16	0·25	<0·2	<0·1	~0·2	~0·9		
C.S.I.R. Cathode	6·0	0·83	7·0	28	18	0·46	<0·2	~0·04	~0·3	~0·7	4H	Tobacco,
Mac. I.		1·20	12·5	50	18-62		<1·0	0·1	2·0			healthy.
Chem. Service		0·8	2·1	43				0·2				
C.S.I.R. Anode	56	1·74	11·6	48	83	1·53	0·53	<0·3	1·4	1·1		
C.S.I.R. Cathode	20	1·91	12·1	76	65	2·0	<0·2	<0·05	~0·8	~0·5	4I	Tobacco, sick.
Mac. I.		2·90	17·0	45	34-84	4·0	2·5	0·18	2·0			
Chem. Service		2·2	13·3	60				0·5				
C.S.I.R. Anode	54	<0·3	1·7	53	54	1·54	2·1	<0·3	93	134		
C.S.I.R. Cathode	34	0·2	1·6	54	70	1·4	1·1	~0·11	59	54	4J	Rumen conte
Mac. I.		1·00	2·5	105	118-284	5·0	5·0	0·45	40			(cattle).
Chem. Service		0·5	2·1	25				1·4				
C.S.I.R. Anode	2·1	0·66	2·5	27	51	1·2	0·70	<0·3	1·1	2·2		
C.S.I.R. Cathode	2·4	0·64	3·5	28	43	1·5	0·5	0·18	1·1	~0·8	4K	Grass.
Mac. I.		1·1	3·8	40	47-66	2·2	<1·0	0·40	2·0			
Chem. Service		0·9	3·8	18				1·0				
C.S.I.R. Anode	<0·05	<0·3	0·14	148	0·5	0·09	1·5	1·6	4·6	3·5		
C.S.I.R. Cathode	<0·05	0·14	0·2	149	0·4	—0·03	1·4	2·3	2·2	2·0	4L	Liver (cattle).
Mac. I.		0·32	0·9	240	1·2		4·0	1·4	8·0			
Chem. Service		0·3	0·3	190				3·7				

lines on the position of the cathode image in relation to the diaphragm opening, and it is possible that the variable results determined at the Macaulay Institute might be associated with this effect.

Vanadium: Both methods give comparable results which, in the majority of cases, agree with those obtained at the Macaulay Institute. In three cases 4B, 4H and 4I the three methods give different results.

Tin: The results are very unsatisfactory when calculated on a percentage basis. The tin concentrations are, however, very low and the methods are evidently not sufficiently sensitive for such small concentrations.

Molybdenum: Agreement between the results obtained in this laboratory and those obtained at the Macaulay Institute is fair. The chemical results are consistently higher than either of these.

Lead: The results obtained in this laboratory are very much lower than those given by the Macaulay Institute. The validity of the former was, however, proved as follows: To three 20 g. portions of sample 4G, O, 3·3 and 6·6 p.p.m. lead were added. These were ashed and analysed by the anode method. The three portions were found to contain 2·2, 5·7 and 9·2 p.p.m. lead. This seems to prove the values of the Macaulay Institute for lead are too high.

CONCLUSIONS

From the above considerations regarding the suitability of the cathode or anode method of excitation of trace element oxide concentrations the following general conclusions may be drawn:

(i) Accuracies obtainable by the two methods of excitation are about the same.
(ii) The alignment of the anode arc is less critical than that of the cathode.
(iii) Because low cobalt and molybdenum concentrations are as common as high ones, the cathode method appears to be more suitable for this type of analysis.

The cathode method of excitation is accordingly preferred for the analysis of trace elements in plant materials when the concentration procedure, originally proposed by Mitchell[9], is used.

The results given in table II also stress the importance and value of interlaboratory collaboration. An adequate stock of homogeneous ashed plant material should be collected and made available to spectrochemists and chemists doing trace element analyses. Such interlaboratory checking will improve considerably the quality of routine trace element results.

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National Physical Laboratory,
C.S.I.R.,
Pretoria.

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VERGELYKING VAN ENKELE KATALISATORE VIR DIE KJELDAHL-STIKSTOFBEPALING

deur

D. F. LOUW

SUMMARY

Under identical reaction conditions HgO (red) in a fairly high concentration, has considerable advantages over Se or $CuSO_4 \cdot 5H_2O$ as a catalyst for the mineralisation of nitrogen.

OPSOMMING

As katalisator vir die mineralisering van stikstof is 'n hoë konsentrasie HgO (rooi) verkieslik bo Se of $CuSO_4 \cdot 5H_2O$ onder gelykwaardige omstandighede.

Verskeie pogings is reeds aangewend om die tydrowende Kjeldahl-metode vir stikstofbepaling te verkort, veral deur versnelling van die verteringsproses en uitskakeling van 'n lang na-verhittingsperiode. Die Wilfarth-Gunning-metode [1] word algemeen toegepas en word aanbeveel deur die „Association of Official Agricultural Chemists" (A.O.A.C.). Dit is egter opmerklik dat 'n betreklik nuwe verbetering deur Perrin [2] nog so weinig praktiese toepassing in analitiese laboratoria geniet. Volgens laasgenoemde metode word 'n kwikkonsentrasie gebruik wat viermaal so hoog is as deur die A.O.A.C. aanbeveel, en die totale reaksieperiode word verminder na minute i.p.v. die gebruiklike ure.

Soos Perrin reeds aangedui het, is die hittetoevoer en konsentrasie van reagense tydsbepalende faktore en moet steeds vir afsonderlike tipes van analise en apparaat gestandaardiseer word.

Wat die reagense betref, het ons enkele varanderings aangebring nl.

(i) Glaskorrels word as kooksteentjies gebruik.
(ii) Kommersiële NaOH word gebruik. Los op in water (1 : 1) en dekanteer die helder oplossing nadat dit 'n paar dae gelaat is om te besink.
(iii) As indikator work 'n mengsel van metileenblou en metielrooi direk by die 4% boorsuuroplossing gevoeg.

METODE

Die „kooktoets" vir die elektriese elemente wat vir die vertering gebruik word, is 7·5 min. (volgens die definisie van Perrin).

As stikstofhoudende verbinding word die betreklik moeilik-verteerbare nikotienamied (nie suiwer nie) gebruik. Hiervan word 0·10-0·12 g. verteer in 'n mengsel van die volgende reagense:

10 g. K_2SO_4 (lae stikstofgehalte),
1·5 g. katalisator (HgO (rooi), of Se (amorfe poeier), of $CuSO_4 \cdot 5H_2O$),
15 ml. kons. H_2SO_4,
+3 glaskrale.

Die mengsel word op vol hitte verwarm totdat die terugvloeiende suur die bek van die fles bereik, waarna die hittetoevoer verminder word tot „4" op die *Simmerstat*-reguleerder.

Reaksieperiodes van 15-180 min. word toegelaat en na 30 min. afkoeling word die mengsels verdun deur versigtige toevoeging van 250 ml. kraanwater. Die ammoniak wat afgedistilleer word nadat sterk alkalies gemaak is met 50 ml. 50% loog, en 5 gm. $Na_2S_2O_3 \cdot 5H_2O$ en twee korrels suiwer sink bygevoeg is, word opgevang in

25 ml. 4% boorsuur+indikator. Deur titrasie met N/10 H_2SO_4 word die ammoniak bepaal. Vir elk van die katalisatore word ook 'n kontrolebepaling uitgevoer.

Onderstaande tabelle bevat die resultate wat verkry is met die drie katalisatore vir die verskillende reaksieperiodes. Die gemiddelde % N is grafies voorgestel teen die reaksietyd.

I Met HgO

Tyd	% N	Gem. % N
15 min.	18·20, 18·89, 19·22	18·77
20 „	18·20, 18·89, 19·22	18·77
25 „	21·69, 21·57, 21·93	21·73
30 „	21·65, 22·00, 21·86	21·84
35 „	21·84, 21·72, 21·70	21·75
45 „	21·66, 21·84, 21·63	21·71
60 „	21·48, 21·58, 21·71	21·59
120 „	21·29, 21·53, 21·62	21·48

II Met Se

Tyd	% N	Gem. % N
30 min.	16·92, 16·53, 15·87	16·44
45 „	18·15, 18·12, 17·57	17·95
60 „	19·26, 19·05, 19·25	19·19
70 „	19·95, 20·19, 19·85	20·00
80 „	19·77, 19·85, 19·49	19·70
90 „	19·84, 19·56, 19·80	19·78
100 „	19·32, 19·26, 19·82	19·47
120 „	18·64, 18·50, 18·47	18·54

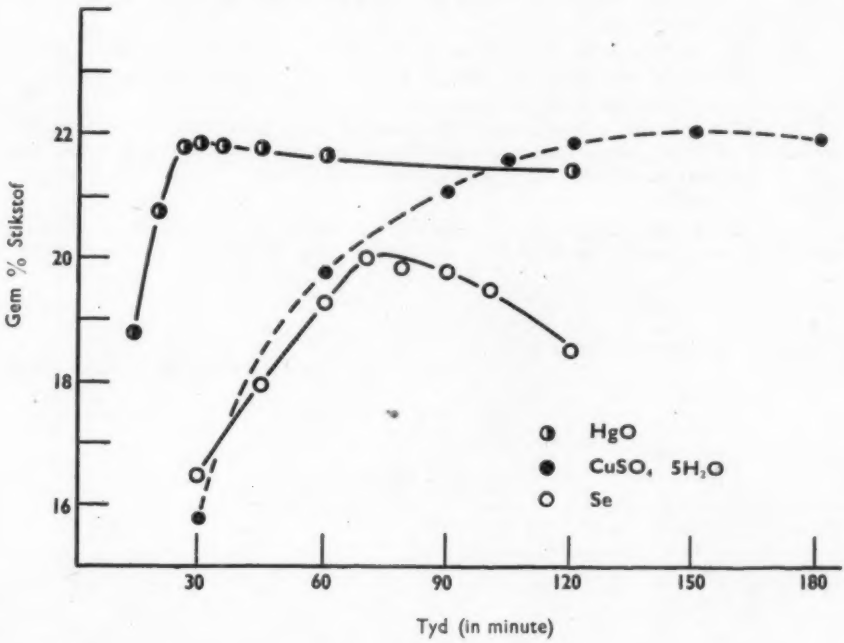
III Met $CuSO_4 \cdot 5H_2O$

Tyd	% N	Gem. % N
30 min.	15·49, 15·99, 15·82	15·77
60 „	19·94, 19·50, 19·88	19·77
90 „	20·88, 21·26, 21·24	21·13
105 „	21·60, 21·71, 21·51	21·59
120 „	21·84, 21·85, 21·89	21·86
150 „	22·10, 22·14, 21·96	22·07
180 „	21·89, 21·94, 22·14	21·99

In 'n afsonderlike reeks bepalings is porsies van 0·2-0·25 g. chemies rein (99·95%) 8-hidroksichinolien geanaliseer vir stikstof met HgO as katalisator. Die betroubaarheid van die metode en die reproduseerbaarheid van resultate blyk duidelik uit onderstaande tabel.

Tyd	% N	Gem. % N
25 min.	9·48, 9·53, 9·59	9·53
30 ,,	9·42, 9·43	9·43
35 ,,	9·44, 9·47, 9·44	9·45
40 ,,	9·45, 9·50, 9·42	9·46
45 ,,	9·35, 9·41, 9·37	9·38
·50 ,,	9·39, 9·41, 9·39	9·38

Teoreties is % N=9·58



Analise van biologiese materiaal

Perrin het reeds opgemerk dat 'n nog hoër konsentrasie HgO en/of K_2SO_4 die reaksie nog meer versnel. By die analise van faeces is dit egter 'n nadeel, want die reaksie verloop dan geweldig vinnig en veroorsaak 'n oormatige opbruising wat maklik die mengsel kan laat oorkook. Selfs wanneer 4-8 g. faeces in 40 ml. kons. H_2SO_4 verteer word met 1·5 g. HgO en 10 g. K_2SO_4, verloop die oksidasie soms nog baie vinnig, maar bedaar spoedig as die hittetoevoer enkele oomblikke afgeskakel en dan weer aangesluit word. Reeds na 30 min. op volle hitte word die mengsel helder en met 'n na-verhitting van nog 30 min. is dit gereed vir distillering.

Monsters van bv. 100 ml. urien (gepreserveer met 10% H_2SO_4), of 1·5 g. gedroogde brood, of rot-rantsoen, of 0·3-0·5 g. vismeel, of 0·1-1·0 g. suiwer stikstofhoudende chemiese verbinding word net so behandel soos aangegee vir nikotienamied met 'n na-verhitting van 20-25 min., d.w.s. nadat die reaksiemengsel helder geword

het. Soms is dit egter wenslik (by aanwesigheid van baie organiese materiaal) om die swaelsuur na 20 ml. te vermeerder.

In gevalle waar groot hoeveelhede amoniak afgedistilleer word (tritasie>25 ml. $N/10H_2SO_4$) is dit nodig om meer as 25 ml. boorsuur te gebruik om dit in op te vang.

BESPREKING

In vergelyking met $CuSO_4 \cdot 5H_2O$ en Se bied die hoe konsentrasie HgO die volgende voordele:

(a) Die algehele mineralisering van stikstof verloop baie vinniger;

(b) 'n Oormatige lang reaksieperiode het slegs 'n geringe daling in % N tot tot gevolg (vergelyk met Se);

(c) Die resultate wat met HgO verkry word, is vir praktiese doeleindes net so goed as dié wat met $CuSO_4 \cdot 5H_2O$ verkry word en baie beter as met Se.

Die metode lewer goeie duplikaatresultate.

As nadele van die gebruik van HgO moet genoem word dat hierdie reagens duurder is as $CuSO_4 \cdot 5H_2O$ (maar nog goedkoper as Se) en dat dit die gebruik van natriumtiosulfaat meebring. Die tydsbesparing, veral by roetinewerk, vergoed egter ruimskoots hiervoor.

Dank word erken aan M. C. Aucamp vir hulp in die uitvoering van die eksperimentele gedeelte en aan die W.N.N.R. vir toestemming om hierdie verslag te publiseer.

Nasionale Voedingnavorsingsinstituut,
Pretoria.

Ontvang 31 *Januarie* 1955.

VERWYSINGS

[1] *Official Methods of Analysis of the A.O.A.C.*, 7e Uitg. 1950, p. 13.
[2] Perrin, C. H. *Anal. Chem.* 1953, Vol. 25, p. 968.

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